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TECHNICAL METHODS OF CHEMICAL ANALYSIS

WORKS BY GEORGE LUNGE, Ph.D., Dr.Ing.

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TECHNICAL METHODS
OF
CHEMICAL ANALYSIS

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VOLUME I.—PART I.

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1908

PREFACE

A revised edition of Dr F. Böckmann's *Chemisch-technische Untersuchungsmethoden*, edited by Professor G. Lunge, was published in 1899, and very soon became recognised as a standard work on the subject. A considerable time had elapsed since the last edition by Dr Böckmann was issued, and the interval had been one of rapid progress in all branches of chemical industry. Professor Lunge's revised version appeared therefore as practically a new book, extended in material and in scope, and adapted to modern methods of work. In 1904 a second edition was called for, in which the whole of the subject matter was thoroughly revised and brought up to date.

The plan of the book consists in the treatment of the technical methods of analysis, applicable to specific industries, in separate sections; all the important inorganic and organic industries are dealt with, and each section has been written by a contributor fully and practically acquainted with the subject. The chief methods of analysis are given in all cases, but full details are described only for those methods which have proved good and reliable in the hands of the writers of the various sections, or which are otherwise recognised as efficient. So far as possible, each section is similarly arranged, the raw materials being treated of first, then intermediate products and methods of control in working, and then final products. A general introduction on analytical methods is included in Volume I., in which the more common operations and apparatus are dealt with.

The English translation has been made from the second German edition.

As the industrial processes, methods of analysis, and legislative conditions are, in many respects, different in this country from those obtaining abroad, almost all the sections have been submitted to experts for revision, so that the English translation has thus been thoroughly adapted to English conditions of manufacture, by specialists fully familiar with the methods of work in use in this country. The contents of each section have been brought well up to date by this revision, and special care has been taken to include references to English work and literature.

This revision has been made as complete as possible, without materially extending the subject matter of the several sections. In a few instances portions of the German text have been omitted, owing to their being inapplicable to the conditions of work here; in such cases the omission is noted in the translation, and a reference is given to the original text. Such further additions as were necessary to bring the contents of the book up to date, since the publication of the second German edition, have been added to the English translation by Prof. Lunge and by the Editor.

The book will be issued in three volumes, and a full index will be provided with each volume. A bibliography of books of reference is appended to each section, and all important tables, in addition to being printed in the text, are also printed for reference at the end of each volume.

With the exception of those cases in which empirical factors are employed in technical work, all the numerical data are calculated from the table of atomic weights for 1908, issued by the International Committee, with $O = 16$ as the basis. The numerical data for gases and for the weights of substances to be taken for analysis so as to correspond to definite volumes of gases, are all calculated from the *real* litre weights according to the most reliable determinations, not from the calculated values. All temperatures are given in centigrade degrees, except where otherwise stated.

The Editor desires to record his thanks to Dr W. E. Adeney for the description of his apparatus for the extraction and analysis of the gases dissolved in water, and for analytical data of the dissolved gases in water, included in the section on "Drinking Water and Water Supplies"; to Dr R. T. Glazebrook, F.R.S., Director of the National Physical Laboratory, for permission to include the methods and conditions adopted by the National Physical Laboratory for the testing and calibration of glass vessels, included in the section on "General Methods used in Technical Analysis"; to Dr W. H. Sodeau for the description of his apparatus for gas analysis, and for kindly reading the section on "Technical Gas Analysis"; and to the Engineering Standards Committee for their permission to include the data from their "British Standard Specification for Portland Cement," and to reproduce the illustrations of the forms of apparatus recommended, in the section on "Calcareous Cements." The Editor is also indebted, for the loan of blocks, to Messrs Brady & Martin, Newcastle; Messrs Griffin & Sons, London; and to Dr H. Seger and E. Cramer of Berlin.

CHARLES A. KEANE.

LONDON, *August* 1908.

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General Methods used in Technical Analysis.

By Prof. G. LUNGE, Ph.D., Dr.Ing., Zürich.

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Revised by C. A. Keane, D.Sc., Ph.D., Principal and Head of the Chemistry Department, The Sir John Cass Technical Institute, London.

LIST OF ABBREVIATED TITLES OF JOURNALS

Journal.	Abbreviation.
American Chemical Journal	Amer. Chem. J.
Analyst	Analyst
Annalen der Chemie	Annalen
Annalen der Physik	Ann. Physik
Annales de Chimie et de Physik	Ann. Chim. Phys.
Archiv der Pharmacie	Arch. Pharm.
American Journal of Science	Amer. J. Sci.
Berichte der deutschen chemischen Gesellschaft	Ber.
Biedermann's Centralblatt für Agricultur Chemie	Biedermann's Centr.
Brewer's Journal	Brewer's J.
British and Colonial Druggist	Brit. and Col. Drug.
Bulletin de l'Association Chimique de Sucre et de Distillerie	Bull. Assoc. Chim. Sucr.
Bulletin de la Société Chimique de Belgique	Bull. Soc. Chim. Belg.
Bulletin de la Société Chimique de Paris	Bull. Soc. Chim.
Bulletin de la Société Industrielle du Nord de la France	Bull. Soc. Ind. Nord
Bulletin de la Société Industrielle de Mulhouse	Bull. Soc. Ind. Mulhouse
Chemical News	Chem. News
Chemical Trade Journal	Chem. Trade J.
Chemiker Zeitung	Chem. Zeit.
Chemiker Zeitung Repertitorium	Chem. Zeit. Rep.
Chemische Industrie	Chem. Ind.
Chemische Revue über die Fett-und Harz-Industrie	Chem. Rev. Fett-Ind.
Chemisches Centralblatt	Chem. Centr.
Chemist and Druggist	Chem. and Drug.
Comptes-Rendus hebdomadaires des Séances de l'Acadamie des Sciences	Comptes rend.
Dingler's polytechnisches Journal	Dingl. polyt. J.
Electrician	Electrician
Electrochemical and Metallurgical Industry	Electrochem. Ind.
Engineer	Engineer
Engineering	Engineering
Engineering and Mining Journal	Eng. and Min. J.
Färber-Zeitung	Färber-Zeit.
Fischer's Jahresbericht	Fischer's Jahresber.
Gazzetta Chimica Italiana	Gazz. chim. ital.
Gerber	Gerber
Gummi-Zeitung	Gummi-Zeit.
India-Rubber Journal	India-rubber J.
Journal de Pharmacie et de Chimie	J. Pharm. Chim.
Journal für Gasbeleuchtung und Wasserbesorgung	J. Gasbeleucht.
Journal für praktische Chemie	J. prakt. Chem.
Journal of Gas Lighting	J. Gas Lighting
Journal of Physical Chemistry	J. Phys. Chem.
Journal of the American Chemical Society	J. Amer. Chem. Soc.
Journal of the Chemical Society	J. Chem. Soc.
Journal of the Chemical Society, Abstracts	J. Chem. Soc. Abstr.
Journal of the Chemical, Metallurgical, and Mining Society of South Africa	J. Chem. Met. Soc., S. Africa
Journal of the Franklin Institute	J. Franklin Inst.

Journals.	Abbreviations.
Journal of the Institute of Brewing	J. Inst. Brewing
Journal of the Institution of Mechanical Engineers	J. Inst. Mech. Eng.
Journal of the Society of Arts	J. Soc. Arts
Journal of the Society of Chemical Industry	J. Soc. Chem. Ind.
Journal of the Society of Dyers and Colourists	J. Soc. Dyers and Col.
Leather Trades Review	Leather Tr. Rev.
Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West	Mitt. k. Materialprüf.
Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen	Mitt. Centralst. Wiss.-tech. Unters.
Mittheilungen des technischen Gewerbemuseums in Wien	Mitt. techn.-Gew. Museums
Monatshefte für Chemie der kaiserlichen Akadamie der Wissenschaften, Wein	Monatsh.
Moniteur Scientifique	Monit. Scient.
Paper and Pulp	Paper and Pulp
Papier-Zeitung	Papier-Zeit.
Petroleum Review	Petrol. Rev.
Pharmaceutical Journal	Pharm. J.
Pharmaceutisches Centralblatt	Pharm. Centr.
Philosophical Magazine and Journal of Science	Phil. Mag.
Philosophical Transactions of the Royal Society	Phil. Trans.
Proceedings of the American Electrochemical Society	Proc. Amer. Electrochem. Soc.
Proceedings of the American Institute of Mining Engineers, and also Bulletin	Proc. Amer. Inst. Min. Eng.; Bull. Amer. Inst. Min. Eng.
Proceedings of the Faraday Society	Proc. Faraday Soc.
Proceedings of the Institution of Civil Engineers	Proc. Inst. Civ. Eng.
Proceedings of the Institution of Mining and Metallurgy	Proc. Inst. Min. and Met.
Proceedings of the Royal Society	Roy. Soc. Proc.
Revue Générale des Matieres Colorantes	Rev. Gen. Mat. Col.
Receuil des travaux chimiques des Pays-Bas et de la Belgique	Rec. trav. chim.
Scientific American	Scient. Amer.
Stahl und Eisen	Stahl. u. Eisen
Tonindustrie Zeitung	Tonindustrie Zeit.
United States Consular Reports	U.S. Cons. Reps.
Zeitschrift der analytischen Chemie	Z. anal. Chem.
Zeitschrift für angewandte Chemie	Z. angew. Chem.
Zeitschrift der anorganischen Chemie	Z. anorg. Chem.
Zeitschrift des Vereins der deutschen Zucker-Industrie	Z. Ver. deut. Zuckerind.
Zeitschrift des Vereins für deutsche Ingenieure	Z. Verein. deutsch. Ingen.
Zeitschrift für chemische Apparatenkunde	Z. für chem. Apparatenkunde
Zeitschrift für das gesammte Brauwesen	Z. ges. Brauw.
Zeitschrift für Elektrochemie	Z. Elektrochem.
Zeitschrift für Farben-und Textil-Chemie	Z. Farb.-u. Text.-Chem.
Zeitschrift für physikalische Chemie	Z. physik. Chem.
Zeitschrift für Spiritusindustrie	Z. Spiritusind.
Zeitschrift für Untersuchung der Nahrungs-und Genussmittel	Z. Unters. Nahr. u. Genussm
Zeitschrift für Zuckerindustrie in Böhmen	Z. Zuckerind. Böhm.
West Indian Bulletin	West Ind. Bull.
Wochenschrift für Brauerei	Woch. f. Brau.

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GENERAL METHODS USED IN TECHNICAL ANALYSIS

GENERAL METHODS USED IN TECHNICAL ANALYSIS

By Professor G. LUNGE. English translation revised by CHARLES A. KEANE, M.Sc., Ph.D.

INTRODUCTION

TECHNICAL methods of chemical analysis have always included many general analytical methods which were introduced as they gradually developed for scientific purposes, as well as certain practical tests which originated for the most part either accidentally or in imitation, on the small scale, of the manufacturing processes of chemical industry. On the other hand, whole classes of operations which now form a considerable part of general analytical chemistry were originally devised and looked upon as purely "technical" methods. This is particularly true of volumetric analysis, which, founded as early as 1795 and 1806 by Descroizilles, was first used as a method for controlling and estimating the value of technical products such as acids and alkalis. Gay-Lussac's methods for chlorimetry (1824), alkalimetry (1828), and for the estimation of silver (1832), as well as the permanganate method of estimating iron introduced by Margueritte (1846), fall in the same category, and were all devised to meet the requirements of technical work, and were at first employed exclusively for this purpose.

Up to the middle of the last century, and still later in many instances, "volumetric" analysis was unrecognised in the course of instruction given in university laboratories: it was regarded with a certain degree of contempt as a "technical" method, the study of which could only be disadvantageous to the attainment of scientific accuracy by students. This view could, however, no longer be upheld after it was shown by Bunsen, in his paper on volumetric analysis by means of iodine (1853), that the accuracy of this process was greater than that of most gravimetric methods, and after other investigators, especially H. Schwarz (1850) and Friedrich Mohr (from 1855), had extended and developed the province of this branch of analysis.

Text-books of general analytical chemistry and introductory works on the subject were at that time the only sources of information available for technical analysis; these were restricted, however, to the gravimetric methods of mineral analysis, elementary organic analysis, and a few volumetric processes. Methods for the examination of products of chemical industry and of associated manufactures were, if published at all, scattered in all kinds of books and journals, and were only accessible at the cost of considerable labour, and then with but very indifferent success.

The publication by Bolley, in 1853, of his text-book of technical methods of chemical analysis was accordingly heartily welcomed; it was almost sold out within a year, but a second edition was not published until 1861. Nearly half of this book of 475 pages is taken up with a short sketch of general analytical operations, methods, and apparatus, and with qualitative and quantitative mineral analysis, treated on the same lines as in every work on analytical chemistry of that period; the second and rather larger part of the book dealt with the analysis of gunpowder, bleaching materials, soils, colouring matters, fuels, fats, oils, illuminants, soap, beer, wine, sugar, milk, tea, coffee, textile fabrics, tanning materials, manures, specific gravity determinations, etc.

In spite of its modest scope, Bolley's book was one of great importance and value at the time of its publication, insufficient as it appears to our present conceptions. It, moreover, indicated a new field of work, and introduced a fundamental principle which must still be recognised, and which was expressed by Bolley in the following words in the preface to the second edition of his book:—

. . . "On the other hand, no artifice, however empirical or wanting in scientific basis, should be despised which, according to reliable information or from personal experience, presents marked characteristics. In fact, it lies in the nature of the case, and therefore I do not consider it necessary to defend it, that certain methods of analysis are made use of which are in some respects untrustworthy. I am not unaware of the objection, which however I consider quite unfounded, that the propagation of such methods is detrimental to science. The latter will certainly not allow itself to be thereby diverted from the search for more rational and accurate methods of analysis, whilst all chemists who are concerned with the investigation of commercial preparations or of industrial products must in very many cases welcome every method of examination, even if it is only of a tentative nature."

This view, that methods may and must be employed in "technical analysis" which cannot be justified from a purely scientific standpoint, still holds; the use of such methods is only justified as a temporary expedient, and therefore only until they are replaced by better and more rational processes. It is scarcely necessary to add that the efforts of all concerned should always be directed towards the attainment of this object, and a great deal has been accomplished in this respect during the half century which has elapsed since the publication of the first edition of Bolley's book. But even now and in the future, very many analytical methods will always be in use for technical purposes which do not find, and ought not to find, a place either in text-books of scientific chemical analysis or in the methods taught in university laboratories. The methods of technical analysis have developed independently in accord with the unavoidable specialisation that has arisen in all branches of science, and they cannot, for the most part, be fitted into the ordinary course of study which long experience has established with tolerable uniformity as the most fitted for instruction in analytical chemistry. This is especially so in respect to the technical examination of organic products and processes; purely empirical methods are often quite unavoidable, although many others with a thoroughly scientific basis are also employed.

The necessity of controlling and regulating the practical operations of works by means of chemical analysis also calls for special consideration. In this case scientific accuracy is usually of no importance whatever; even were it attainable, it would have no greater value for the control of the working than an approximate estimation. It is, on the contrary, of far greater importance to obtain the analytical results as rapidly as possible, in order that the working conditions may be regulated accordingly. In such cases, which are of very frequent occurrence in technical work, lengthy analytical methods are quite excluded; even if a whole army of highly-trained scientific analysts were employed, were this practicable, their reports would come "after the fair," and would therefore be quite worthless, whilst simple tests rapidly carried out by an empirical "tester" give the manager all needful information. Any great degree of accuracy is usually neither attainable nor necessary in such instances. There are, however, some cases in which rapidity and some degree of accuracy must be combined, and this is successfully attained by "testers" through constant practice; the accuracy attained by workmen exclusively devoted to one branch of testing is often such as to command the admiration of the trained chemist whose work is conducted at leisure in his laboratory. This is the case, for instance, in iron-works, and the degree of certainty in the quality of the product attainable nowadays in this industry is in great part to be ascribed to the development of technical methods of analysis, which combine extreme rapidity with astonishing accuracy.

In the analytical work concerned with the purchase of raw materials and with the sale of manufactured products, the chemist has usually more time, although by no means unlimited time, at his disposal. Here again, the nature of the product often necessitates the employment of more or less rough empirical methods, but if better and more exact methods are available they should certainly be preferred. An accuracy and certainty in analysis such as would be regarded even in purely scientific laboratories as very good work, is often required of a works chemist, by whom it can only be attained as the result of constant practice.

The technical methods of chemical analysis comprise the following classes of work:—

1. Examination of Raw Materials

Accurate methods of analysis are frequently employed. In other cases, rougher tests may be sufficient within limits, and in part must suffice in default of better methods; physical, microscopic, or other external methods of examination are also often used.

2. Control of Working Conditions

Chemical analysis, with the addition, in many cases, of other methods of a non-chemical character (*e.g.*, specific gravity determinations, pressure relations, etc.), are adopted. The methods usually employed are those which can be carried out with the greatest possible rapidity, and are consequently often lacking in accuracy.

3. Examination of Final Products

Accurate methods of analysis are sometimes employed, especially when a guarantee of composition is required; frequently, however, easily observable external characteristics suffice.

In all three classes different methods of examination may be necessary, namely:—

(*a*) **Qualitative tests,** which are in most cases concerned with the detection of an impurity.

(*b*) **Quantitative determination of a principal constituent,** which is the subject of a guarantee in buying or selling, or which is a leading factor in the working of a process.

(*c*) **Quantitative determination of secondary constituents,** in which various considerations demand attention, namely:—

- (*α*) Secondary constituents of value which form the subject of a guarantee, such as the percentage of carbon in steel.
- (*β*) Secondary constituents which are deleterious impurities, and which ought not to exceed a certain maximum, *e.g.*, phosphorus in steel, chlorides in potassium nitrate.
- (*γ*) Secondary constituents the estimation of which serves for the indirect determination of the amount of the principal constituent present, as in the valuation of Chili saltpetre.

(*d*) **Quantitative determination of several constituents,** usually a combination of the two classes *b* and *c*, *i.e.*, the estimation of the chief constituent and of one or more important impurities, as the estimation of the alumina, iron, and free acid in the analysis of aluminium sulphate, and the determination of the iron, sulphur, and phosphorus in the examination of iron ores.

(*e*) **Examination of certain quantitative or qualitative effects produced by the substance,** *e.g.*, the tinctorial power of dyes, the viscosity of lubricating oils, the flash-point of petroleum.

(*f*) **Examination of certain external properties demanded by the trade,** such as, colour, lustre, density, strength, etc.

(*g*) **Complete chemical analysis** is only very exceptionally required for technical purposes; it may be necessary in such instances as a new discovery of ores and the like.

These various classes of analytical work are all dealt with in this book; they are considered under the several sections dealing with the various industries into which the subject matter is divided, according to their nature. A general knowledge of analytical chemistry, and more especially of mineral analysis and of elementary organic analysis, is premised. The description of special apparatus and methods of work is in all cases directed to the conditions that are requisite or useful for the attainment of the results that are required in technical work, even in those instances in which general methods of analysis are employed. The greater part of the book is, however, naturally devoted to the methods which have been specially worked out for technical purposes, and which are but seldom if ever practised in scientific laboratories.

The work is divided into a general and a special part. In the former, the methods and apparatus described are of a general character, such as are used for a variety of purposes, particular stress being laid upon those considerations that serve to facilitate the work of technical laboratories. The more specific applications of these general processes is dealt with in the special part of the book in which the analytical methods are grouped, under the headings of the products concerned with the various branches of chemical industry.

I.—GENERAL OPERATIONS

The Taking of Samples

The taking of samples is a problem of some difficulty, and is one which is practically outside of the domain of the purely scientific analyst, who often fails to recognise its importance; the technical chemist who has not had a scientific training is still more frequently, perhaps, ignorant of its difficulties, so that serious errors and heavy losses ensue. The preparation of an average sample, really representative of the quality of the material to be investigated, requires special care and precautions. It has happened, for example, that a piece of marl from a quarry was given to an analyst in order to ascertain its suitability for the manufacture of cement, and that an accurate analysis of the piece was made, and conclusions drawn from the results as to the suitability of the whole material in the quarry for this purpose!

Even in much simpler cases the difficulty of obtaining a fair average sample is often not sufficiently realised by those concerned. How easy it is, for example, to make a considerable error in taking a sample of coal, if a large piece of pyrites finds its way into the sample—or conversely. But even in taking samples of powdered materials, serious errors or intentional deception may occur, if all necessary precautions are not taken.

The preparation of a really average sample is most difficult in the case of materials occurring in large pieces; it is considerably easier with more finely grained materials, still easier with powdered materials, easiest of all, as a rule, with liquids, and more difficult with gases. Special difficulties occur when contact with air, whilst the sample is being taken and ground, may alter its condition by evaporation, absorption of water, oxidation, etc. In such cases very special precautions are necessary, which will be fully dealt with subsequently.

The most accurate analysis is, of course, worthless, and endless mistakes and disputes must arise, if the samples are not properly taken; it is therefore essential to expend as much care on sampling as on the analytical work in the laboratory.

As already stated, sampling is most difficult in the case of materials occurring in lumps, and this is especially the case when the valuable constituent occurs only in small amount and very unequally distributed, as in ores of the noble metals, or when certain very deleterious impurities, also unequally distributed, are present. The disputes that have arisen from defective sampling have led to the drawing up of definite rules for sampling; also, it has become the custom, in all important cases, for the operations of taking samples, grinding them, and making them into a form ready for handing to the chemist, to be carried out in the presence of representatives of both parties concerned, or in the presence of a mutually appointed referee. Usually several bottles are simultaneously filled with the prepared average sample, and closed with the seal of both parties.

The following directions lay no claim to being a permanent solution of the difficult problem of sampling; they can only represent an approximation, but they are at least as satisfactory as any other plan that is in use. They are founded essentially on the directions contained in *The Alkali Makers' Handbook*, by Lunge and Hurter (second edition, 1891, p. 172 *et seq.*), which were drawn up with the co-operation of a number of experienced manufacturers, and are amplified by the results of further experience.

In many cases, particularly in the industries connected with organic chemistry, but also, *e.g.*, with caustic soda, fuming sulphuric acid, etc., the samples must be taken according to special methods applicable to each individual case, owing to the peculiar nature of the substances in question. The necessary information on these points is given under the individual sections.

Detailed rules for sampling in metallurgical works have been given by Juon;[1] the remarks on sampling by Hintz[2] do not call for any special comment.

A. Materials in Large Pieces

This class includes coal, metallurgical ores, pyrites, pyrolusite, etc., which are usually transported in shiploads, canal boats, or in railway waggons. In case of water-transport, the check sampling takes place as a rule at the port of arrival, during the transfer to the railway waggons, or, in cases where the factory or the foundry receives the goods at its own landing-place, samples are taken there during the unloading into trucks or other transport vessels. In other instances the sample is taken on arrival of the train at the works, either before or during the unloading of the material. In all these cases the sampling can be advantageously combined with the weighing. The taking of samples from a previously unloaded large heap of coarse material is always a very uncertain procedure, and should be avoided whenever possible. Apart from the general difficulties which unavoidably occur in the above-mentioned conditions of sampling, two additional difficulties arise in the last case; on the one hand, changes in the amount of moisture may occur, owing to evaporation, showers of rain, downward percolation of moisture, etc., and secondly, the larger pieces are apt to roll forwards, and thus make the mass still less homogeneous than before.

The larger and the less uniform the pieces of the material in question are, the larger must be the samples taken. It is most important to secure a due ratio between the larger pieces and the finer powder, which is practically always present, since there is often an essential difference in quality between the two.

If the pieces do not exceed a billiard ball in size, and are roughly of the same dimensions, it is sufficient to take a sample from each unit-load[3] by means of a scoop of about 5 kilos (12 lbs.) capacity. If the

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[1] *Z. angew. Chem.*, 1904, 17, 1544.

[2] *Z. f. öffentl. Chem.*, 1903, No. 21.

[3] This term designates the load raised by a crane, carried by a truck, or any other conveyance, by means of which the material is transported from the hold of the ship, etc., to the weighing machine, or to the landing-place.

material is in larger pieces, and especially if not uniform in size, it is preferable to empty a whole unit-load at intervals, *e.g.*, the tenth or twentieth load on the weighing machine, on to a separate place, from which the whole average sample is collected. The greatest possible care must be taken, in sampling by this method, to have the ratio between coarse and fine material represented as accurately as possible in the average sample.

The average sample thus obtained is first crushed to pieces about the size of a walnut. This is done either by hand or by means of a mechanical arrangement such as studded rollers, according to circumstances, care being taken to break down the whole of the coarse pieces, even although it may be troublesome to do so. The roughly broken material is then thoroughly mixed by repeated scooping backwards and forwards, and is then spread out in a flat heap and a smaller sample taken. This is best effected by cutting two stripes crossing each other at right angles out of the whole heap, and adding to this four smaller quantities taken from the middle of each remaining quadrant.

The weight of the sample thus prepared should be at least 10-12 kilos (¼ cwt.); if the material is very uneven in character, considerably more must be taken and special attention must be paid to the precautions described above for obtaining a true average sample. In such cases it is often necessary to repeat the above operation by scooping the first large sample together in a conical heap, spreading it out flat again, and then again cutting two stripes intersecting at right angles, and adding further material from the quadrants as above.

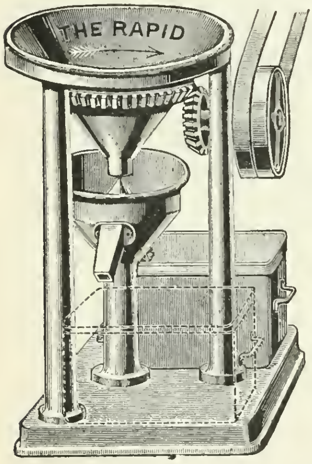

Fig. 1.

Several mechanical samplers have been constructed in order to make this operation simpler and more reliable. Of these the "rapid sampler" of P. Clarkson[1] is largely employed here (Fig. 1). The principle of the machine is to cut out a number of sections of the material as it passes through the apparatus in an annular rotating stream; the relative amounts can be regulated at discretion. This machine can be employed for liquids, powders, and for substances in grains or in large fragments. It is also very suitable for uniformly distributing a sample into bottles.

The reduced sample thus obtained is then further broken up. A mechanical arrangement may also be employed at this stage, but only when it is so arranged that it can be thoroughly cleaned after every

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[1] For a full description, see *J. Soc. Chem. Ind.*, 1894, **13**, 214.

operation. The more common practice is to effect the grinding by hand, usually in a large iron mortar. This is, however, not the best method, because it is not very easy to completely remove the powder from the mortar without loss, and the uniformity of the sample is thus adversely affected ; also, some of the substance may easily remain behind unnoticed in the mortar, and contaminate the next sample. (For arrangements for grinding, *cf.* p. 17.)

To overcome the disadvantages of an ordinary mortar, a flat cast-iron plate, specially constructed for the purpose, 0·8-1 metre square, with a vertical rim 5-10 cm. high, interrupted at one point in order to allow of the powder being easily run out, may be substituted ; these plates should be 20-25 mm. thick, and solidly embedded in a horizontal position to prevent breakage. The sample, previously reduced to pieces not larger than walnuts, is further broken up on the plate with a sledge-hammer, shaken from time to time through a sieve of 3 mm. mesh, and the residual coarse powder repeatedly ground up until it has all passed through the sieve. In this way complete cleanliness can be observed with much greater certainty than by the use of a mortar.

The 10-12 kilos ($\frac{1}{4}$ cwt.) thus obtained are then spread out flat, and a further decreased sample of 1-2 kilos (2 to 4 lbs.) prepared from it by thorough mixing and removal of intersecting stripes, etc., in the same way as before. This is subjected to a further mixing, and the separate samples for analysis are then taken from it, preferably as follows. Three, four, or more wide-mouthed sample bottles holding 100-200 c.c. are placed close together on a sheet of paper ; a handful of the sample is taken, and the hand moved over the bottles in succession, so that some of the substance falls into each. This is repeated until the bottles are quite filled. Manipulation by hand is more reliable than the use of a small scoop, etc. ; in the latter case the coarser particles always roll forward, so that too large a proportion is delivered into the foremost bottles.

When the bottles are full, they are closed immediately with tight-fitting corks, which are cut off straight above the necks of the bottles and carefully sealed. When control samples are taken, the seals of both parties are affixed in such a way that the cork cannot be removed without injuring them.

The powdering, mixing, and filling of the bottles should be carried out as quickly as possible, to prevent the evaporation of water from moist products, or, conversely, to prevent the absorption of moisture (under special circumstances also of oxygen or of carbon dioxide) from the atmosphere.

The analyst, on receiving the sealed bottles, notes the seal, which must, of course, be intact, and the affixed label, opens the bottles, shakes out the contents on to glazed paper, and mixes the sample quickly. If the moisture is to be estimated, a sufficiently large sample, up to

100 g., is taken for this purpose without further grinding. The remainder is ground up until the whole passes through a sieve of 1 mm. mesh. Porcelain or steel mortars are used for the grinding, according to the hardness of the substance. The former would not be suitable for pyrites, for example, because they are attacked to some extent by substances of this degree of hardness, and the sample might be contaminated; on the other hand, iron vessels should not be used for reducing pyrolusite to a fine powder, because some metallic iron might thus find its way into the sample.

Finally, a few grams of the substance which has passed through the 1 mm. sieve is taken, after a further thorough mixing, and reduced by means of an agate mortar to the degree of fineness requisite for analysis; in special cases a steel mortar may be employed.

Since some change in the amount of moisture is almost unavoidable during the final grinding, the final sample is either dried in a drying oven or exsiccator, and then weighed out in the dry condition for analysis, or the moisture is determined separately in another sample and the results calculated on the dried substance. The actual percentage of moisture in the sample is taken from the determination made with the coarsely powdered substance as above, and not from this last determination.

B. Raw Materials in the form of Powder, Dross, etc.

This class includes ores in the form of smalls or slimes, common salt, potassium salts, etc., as well as many other inorganic and organic raw materials. A simplified method of sampling can usually be employed for products of this character, samples being taken from each "unit-load" by means of a scoop of about $\frac{1}{2}$ kilo (1 lb.) capacity; in the case of a railway-waggon load, several samples from different parts, *e.g.*, the front, middle, and back are taken. The separate samples are placed together in a cask and covered over. After the sampling is finished, the contents of the cask are emptied out on a level, clean, hard surface, spread out flat, and the mass scooped together into a cone in the centre by working regularly round the heap with a spade; the heap is again spread out flat and a sample of about a quarter of the mass taken by removing two intersecting stripes with the scoop, and adding to this some material from the middle of each of the remaining quadrants. This operation is repeated with the sample thus obtained, until finally not more than 2 kilos (4 lbs.) is left, which, after being well mixed, is divided among the sample bottles required for the analysis, as described.

In the case of raw materials which arrive in boxes, casks, sacks, etc., the procedure described under C can usually be followed; in fact, the final products of one industry are very frequently the raw materials of another.

C. CHEMICAL PRODUCTS IN THE FORM OF POWDER.

If these are loaded in loose condition, that is in ships' holds, railway waggons, or carts, the sample may be taken as described under B; but it is better to employ an *auger*, especially if the samples have to be taken from stores or from casks or sacks. In the latter case a sample is taken from every fifth, tenth, or twentieth cask or sack, according to the size of the consignment and the probability of inequality in the material; it is to be borne in mind however, that, owing to the action of the air (or possibly owing to deceitful manipulation!), the condition of the outside and superficial portions of the material may differ more or less from that of the interior. It is, therefore, always more reliable to use the auger.

The usual form of this instrument is shown in Fig. 2. It consists of a long borer of stout sheet-iron, with a hollow interior and a longitudinal slit on one side, provided with a handle *a* at the upper end, and with the lower end beaten out to a sharp point *b*.

The use of the auger renders it possible to obtain a sample throughout the whole layer of substance. If a sample is to be taken from sacks or casks, the instrument is used only once for each vessel, but if, on the other hand, it is to be taken from a large heap stored in a warehouse or the like, the auger should be inserted in from six to twelve different places according to the size of the heap. Care must be taken to turn the instrument on its axis when it is lowered into the heaps, casks, etc., for drawing the sample.

This simple form of the auger has several defects. For example, in the sampling of sugar it is quite satisfactory for the purer primary products and even for well separated secondary products, but it is not reliable for moist, syrupy cane sugar, because the column of sugar, on being drawn out, is apt to break off at the lower end of the auger. Consequently, according as the sack is erect or inclined, the sample may represent either the moistest part of the contents containing most syrup, or the best-drained portion. Again, in taking samples of granulated or crystal sugar, it often happens that none of the sugar remains in the sampler.

FIG. 2.

In order to avoid these drawbacks, Gawalowski[1] has constructed an auger which Böckmann recommends from long personal experience. This (Fig. 3) consists of a metal sheath which has a metal bearing suitably soldered to it at B, and in which a quadrangular or triangular steel rod provided with a handle (C), slides. The valve at the lower end of the sampler is movable by means of a hinge, in such a way that in

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[1] *Oest. Zeit. Zuckerind*, 1888, Part V.

position D_1 it allows the substance to be sampled, to enter from below upwards, whilst in position D it prevents the sample from falling out of A. When the auger is pushed into the material, the rod C slides sideways in such a way that the flap is fixed in position D_1, and on with drawing it the rod C releases the flap and the latter is closed by the pressure of the substance in the sack on the attached flange.

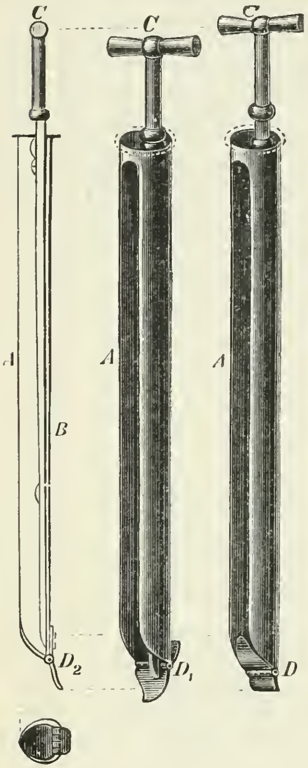

Fig. 3.

Gawalowski's auger works automatically, and samples of material can therefore be taken quickly and safely; it is made of copper or other suitable metal.

Angerstein's[1] auger, a tubular instrument, with the lower part half-open and running to a point at the extreme end, is also to be recommended; it allows of samples being taken from the interior of a vessel without admixture with the upper, altered layers. In whatever way the separate samples may have been taken, they should first be emptied into a box, or, in the case of alterable substances, into a large bottle, which must be kept corked between each addition. The whole contents of the vessel are then thrown out on to a large sheet of paper, thoroughly mixed, any lumps that may be present crushed with a spatula, and then if the quantity is too large a smaller average sample taken, as described above. The samples are then placed in bottles, corked and sealed.

In the case of substances which alter quickly in the air, such as bleaching powder, potassium carbonate, etc., the sample bottles must be kept well closed, and only opened when a new portion of the sample is to be added; similarly, the mixing and distribution of the sample into the bottles must be carried out as quickly as possible.

D. LIQUIDS

The sampling of mobile liquids is a very simple operation, but that of viscous liquids, and especially of sticky, syrupy substances and pasty mixtures, is more difficult. When ordinary liquids are contained in large receptacles, the different layers very often differ in composition.

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[1] D.R.P. 26680.

If, owing to shaking during transport, or from other circumstances, it can be taken for granted that the contents of each individual vessel are uniform, a small sample is taken from every fifth, tenth, or twentieth cask or carboy, etc., by means of a syphon, or as otherwise desired, and an average sample prepared by mixing and shaking. The taking of samples when smaller vessels used for transport are being emptied into a larger receptacle, is very simply effected, by placing a small flask, held by means of a wire (Fig. 4), under the bung-hole or stopcock of the cask, or the mouth of the jar.

Fig. 4.

In the case of large receptacles, where the different layers might vary in quality, the sample is taken by means of a glass tube of suitable length, contracted above and below, the equivalent of a pipette, which is gradually lowered into the liquid, so that a section through the whole depth of the vessel is obtained. In many cases an iron tube, provided with some kind of valve, may be employed for this purpose.

If a sample of a very large quantity of liquid has to be taken, *e.g.*, from a tank-cistern holding 10,000-15,000 kilos (10 to 15 tons), or from a larger reservoir holding 100,000-200,000 kilos (100 to 200 tons), the sampling with the glass pipette or long iron tube provided with a valve at the lower end, must be repeated several times.

Gawalowski[1] has constructed a suitable pipette for liquid and semi-liquid substances, which consists of two iron cylinders, one inside the other, closed at the lower ends, and each having a fairly wide longitudinal slit; they are so connected, by means of a bayonet-slot, that the two longitudinal slits can be made to coincide to form a single closed hollow cylinder, by a simple rotation. The instrument, which is sufficiently long to be able to penetrate all the layers of a large cask, and is provided with a handle at the top, is introduced into the liquid in the closed position and then opened, so that liquid enters uniformly from all levels; the cylinder is then closed, withdrawn, and the contents delivered into a shallow vessel.

For taking samples of the liquid intermediate products of a working process, the specific apparatus is provided with stopcocks or valves, by means of which samples can be taken as often as desired. If, however, an average sample, consisting of a number of single samples taken seriatim without a break, is desired, so-called "dropping-bottles" are employed. These are large jars, holding about 50 litres, into which the liquid drops uninterruptedly. The rate of flow is regulated by means of a valve, and the dropping is controlled by means

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[1] *Oest. chem. u. tech. Zeitschrift*, 6, 197.

of a glass tube attached by a rubber connection, carrying a narrow rubber ring inside at the top, in which a small glass tube drawn out to a fine point is fixed.

Satisfactory average samples of effluents and the like can be obtained by employing a water-wheel revolving in the liquid, by means of which small samples of the liquid are transferred continuously to a reservoir, from which the average sample is taken.

Very concentrated liquids, in the analysis of which possible errors in measuring would have a considerable effect, are often not employed directly for analysis, but are first diluted (*e.g.*, 1, 10, or 20 c.c. to 100, 200, 500, or 1000 c.c.), and an aliquot part of the diluted liquid taken. In many cases, however, it is simpler to measure out such liquids with an accurate pipette, *e.g.*, a 1 c.c. pipette graduated in $\frac{1}{100}$ c.c.

E. GASES

The sampling of gases, which may be either final products, as with illuminating gas, or by-products of industrial processes, as is more frequently the case, is described in the section on "Technical Gas Analysis," and under the individual industries concerned.

THE COLLECTION AND STORAGE OF SAMPLES

In works where the processes go on uninterruptedly, three vessels should always be kept ready for each product of manufacture under analytical control, one of which is allotted for the night-shift and the other two for the day-shift.

The taking of samples in the works is, as a rule, carried out by a workman specially appointed for the purpose, in addition to his other duties. In the morning after six o'clock, he fetches the sample bottles collected during the night, which are distributed at different parts of the works, or he takes the samples, if this has not already been done. All the bottles are put into a wooden "sample box," which contains a number of compartments, and taken into the laboratory. Suppose, for instance, it is seven o'clock in the morning of December 6th. The laboratory boys begin testing the night samples from December 5th to 6th which have just been brought in, as well as the day samples brought in on the evening of December 5th before six o'clock. In the evening the sample collector fetches away the sample bottles brought in the morning as well as the day sample bottles brought in twenty-four hours previously, whilst at the same time he brings the day samples of December 6th.

These samples may be kept on a suitable stand provided with several compartments. Thus over night only the day samples brought in the evening, on the following day the night samples brought in the morning as well, would be accommodated in the stand.

This system of taking samples has the drawback that the results for the day samples are usually obtained fully twenty-four hours after the sampling, whereby in many cases timely measures for correcting the working of the process in question are rendered impossible. An advantageous alternative method is to take the day samples only from six o'clock in the morning till two o'clock in the afternoon, and the night samples from then up to the next morning at six o'clock. The results of the previous night's work are then got at midday, and those of the same day in the evening. This system of taking samples has also its disadvantages, however, because almost half the day is reckoned as night, and therefore irregularities in the working occurring in the afternoon cannot be so easily controlled and located.

These shift-samples, being temporary, are not retained for more that twelve or twenty-four hours respectively. The samples of raw materials and of final products, on the other hand, are usually stored carefully for one or more months (not infrequently sealed), so that they can be referred to in case of dispute. Date of sampling, name of the seller or buyer, percentage of the constituents or of the important constituents found, weight, and method of packing (sacks, casks, etc.), and the number should be entered on the labels as well as in a special laboratory book.

II.—GENERAL LABORATORY OPERATIONS[1]

A. Grinding of Substances

The reduction of a large average sample to a smaller one has already been discussed; the grinding is effected by very diverse methods, and is carried to very different degrees of fineness according to circumstances.

For the coarse powdering of hard substances, such as ores and analogous products, iron mortars holding from 1-20 litres and upwards are suitable, provided contact with iron is not disadvantageous.

A good arrangement for grinding is shown in Fig. 5. Instead of the pestle, there is a heavy almost spherical block, carried on a pivot at the bottom of the mortar, which is moved round by a handle, and which can readily be lifted out.

For substances which form a fine dust, the twofold evil of inconvenience to the operator and loss of material is avoided by fixing a kind of sack round the rim of the mortar; the sack is contracted at the

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[1] *Cf.* H. Benedikt, *Z. angew. Chem.*, 1902, **15**, 78. This paper comprises some interesting considerations, on the non-chemical side, of the arrangement of works' laboratories.

top, where it is firmly bound round the pestle; this precaution is specially to be recommended for poisonous substances.

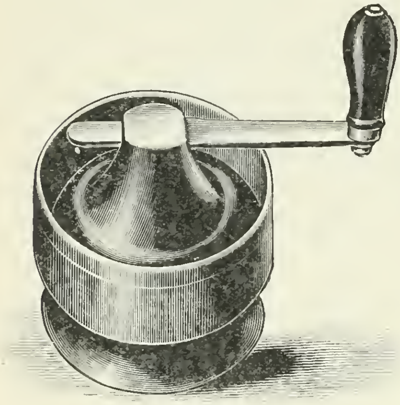

Fig. 5.

It is almost always necessary to pass the material in the mortar through a sieve from time to time, and to powder the coarse residue separately.

For very hard ores and the like, an ore-crusher can be employed with great advantage, such as that shown with the cover open in Fig. 6.

For grinding small amounts of material, the ordinary steel mortar is used; when dust is to be avoided, it is provided with a brass cover, which is screwed on.

In default of a steel-mortar, recourse may be had to the following plan. The pieces of material are wrapped in tough paper of close texture, and broken up on a hard support with a heavy hammer; a little of the substance is lost in this manner, owing to its being beaten into the paper, from which it cannot easily be completely detached.

Less hard substances are usually powdered in porcelain or earthenware mortars; these would give up some of their material to harder substances. Apparatus constructed on the principle of coffee-mills, and made either of earthenware or of iron, are also used.

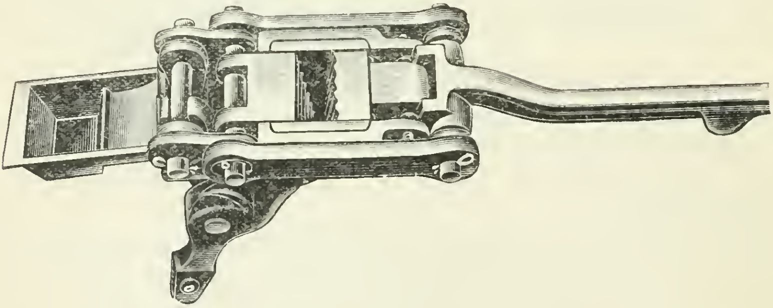

Fig. 6.

In large works where one and the same kind of substance has often to be powdered, mechanical grinding-machines are employed, such as small ball-mills, plain-, ribbed-, or toothed-rollers, apparatus similar to coffee-mills, or small crushers with vertical rollers.

The breaking up of tough substances and of materials of an exceptionally irregular character often requires special apparatus; these are described in the respective sections, but it may be mentioned that cutting-machines working on the lines of a hay or straw chopper, coffee-mills, toothed-crushers, and the like, may often be adapted for this purpose.

All forms of grinding apparatus should be accessible in all their parts for thorough cleaning, and should be cleaned regularly.

Reduction to a fine powder for analysis is effected in agate, porcelain, or steel mortars, according to the nature of the substance, and is, as a rule, combined with rubbing ("bagging") through silk gauze.

B. WEIGHING

A laboratory balance when adjusted should give readings to within 0·1 mg.; the more delicate assay balances are treated of subsequently. The principles of weighing, calibration of weights, etc., are described in the ordinary text-books on analytical chemistry. Rough balances, usually without a glass case, are used for weighing out large amounts of substance. For many purposes an intermediate quality of balance, reading to 1 mg., and provided with a glass case, is very convenient, particularly for weighing out fairly large quantities of material, which are then dissolved and made up to a definite volume, of which an aliquot part is taken for the analysis.

For less accurate work, druggist's hand-scales, with horn scale pans suspended by silk cords, are very useful, the substance being weighed directly into the scale pan. A handy form of this balance is shown in Fig. 7. One arm is graduated in 100 divisions and provided with a sliding weight, so that from hundredths of a gram up to 1 gram can be weighed out directly, whilst larger quantities are balanced by ordinary weights placed in the scale pan.

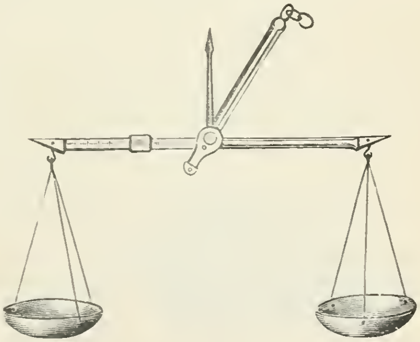
FIG. 7.

These hand-scales are usually only employed for loads up to 30 g. and to an accuracy of 10 mg.; they are also made to carry 100 g. and over.

In using them, they are held above at the handle, so that the silk cords are taut and the scale pans just rest on the table; by then gradually raising the balance a little it is easy to see if it is in equilibrium, and if not, equilibrium is established by means of small pieces of paper, shot, garnets, etc. The substance to be weighed is always placed directly on the pan. If the physical condition of the substance does not allow this to be done, it must be weighed on a simple chemical balance. Hand-scales are not suitable for weighing into beakers, watch-glasses, etc. Their chief advantage is the rapidity gained in the weighing out of dry materials.

For calibrating litre flasks, and for many other purposes, a balance is required which can be loaded up to 2 kilos and turns with 50 mg.; it can be used for many other analytical purposes also, *e.g.*, in the estimation of moisture in coal, coke, salt, etc., where 100 g. or more of substance is weighed out. No matter what kind of balance is employed, the greatest possible rapidity in weighing is always to be aimed at; the necessarily numerous daily analyses cannot possibly be made if five or ten minutes are taken up for each weighing.

Many simple artifices are accordingly made use of to effect this. In weighing on sensitive balances, crucibles, watch-glasses, beakers, etc., the weight of which is known to 1-2 mg., are used, and this weight is written either on the glass itself, or the vessels are marked with successive numbers, and a note of the weights corresponding to the individual numbers recorded. In the weighing of platinum crucibles, etc., which are in frequent use, the actual weighing is really only a check, involving a correction of the weight within the limits of a few mg.

If one and the same vessel is very frequently used in weighing, it is very convenient to cut a tare for it out of copper, nickel, or aluminium foil, which is placed in the other scale pan. With suitable precautions this procedure, which saves much time, may be employed in weighing platinum crucibles for gravimetric analysis.

When the weighing out is not done on the horn scale pan itself, small beakers, watch-glasses, etc., are used, and in the case of alterable substances, stoppered weighing bottles, preferably such as can stand on the pan. Scale pans made of glass, aluminium foil, etc. (Fig. 8), from which the substance can easily be delivered, are very convenient.

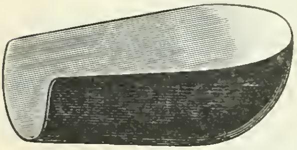

FIG. 8.

Glazed paper is also often used. In all cases the appropriate tare, which should be checked, is placed ready on the other scale pan.

In works laboratories it is exceedingly convenient to have a single weight, made of aluminium or nickle foil, and adjusted by filing down, as the tare for any very frequently occurring quantities. In order, *e.g.*, in the analysis of bleaching-powder (*cf.* p. 22), to be able to read off percentages of available chlorine directly on the burette without calculation, 7·090 g. of the sample must be weighed out; for this purpose a piece of lead of exactly this weight, which is clearly marked on it, is prepared and kept ready in the balance case.

R. Hase[1] has constructed an analytical balance, which, by means of

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[1] *Z. angew. Chem.*, 1898, **11**, 736.

a system of levers, at once gives the weight to a decigram or even to a centigram, so that it is only necessary to complete the adjustment by means of the rider; the complete weighing can thus be very rapidly carried out. This is particularly advantageous for weighing out definite amounts of substance, the desired quantity being obtained directly from the indication of the pointer on the scale, without having to bring the balance to rest.

For the actual weighing off, a small horn, porcelain, or glass spoon is employed, and the number of spoonfuls taken to approximately reach the required weight observed. Daily practice leads to very great skill in this respect, so that the proper weight, to within a few mg., is often hit off at the first attempt.

The weighing out of exactly 0·5, 1, 2, 5, 10, 20, 50 g., etc., has the advantage that the analytical results are easily calculated to percentages; this method can be much recommended, and has been generally introduced in works' laboratories.

In order to transfer the weighed substance completely from the watch-glass, beakers, etc., to the vessel for the analysis, a fine brush with a handle about the size of a penholder is employed; the greater part of the substance is transferred by tapping with the brush, the remainder by brushing the glass.

When the percentage of moisture is to be determined, the substance is weighed directly into the same dish that is placed in the drying oven, and subsequently weighed; deep vessels, such as beakers, are not suitable for this purpose, because they do not sufficiently permit the evaporation of water by renewal of the air. When a substance is to be ignited, it can be weighed directly in the platinum or nickel basin to be used; polished iron basins can be employed if a less degree of accuracy is required.

As shown by J. Wagner,[1] a correction for weighing in air is not necessary, either in respect of the varying specific gravities of the different substances used in volumetric estimations or of the brass or platinum weights used, as the errors are inappreciable.

For very accurate work, weights made of rock crystal are employed; their adjustment requires special precautions.[2]

One very useful method of weighing out which is often employed in technical laboratories, is to weigh out such an amount of substance (or, in certain circumstances a multiple of the amount) that the number of c.c. of volumetric solution used, or, in gas volumetric analysis, the amount of gas evolved, gives a percentage value either without any calculation or by means of a simple mental multiplication or division. Many examples of this are given subsequently, so that the following

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[1] *Massanalytische Studien*, p. 37.

[2] *Cf.* Göckel, *Z. f. chem. Apparatenkunde*, 1905, I. 76.

will suffice as a type of the method. In the analysis of bleaching powder the "available" chlorine is required; Penot's arsenious acid solution is made up to correspond to 0·1 g. molecules, or 3·545 g. chlorine per litre, or 0·003545 g. per c.c. Consequently, $20 \times 0{\cdot}3545$ g. $= 7{\cdot}090$ g. bleaching powder are dissolved in a litre, and 50 c.c. $= 0{\cdot}3545$ g. taken for a titration; then each c.c. of the solution indicates 1 per cent. of available chlorine. For the estimation of calcium carbonate in a sample of limestone by measurement of the evolved gas, since 1 c.c. carbon dioxide at 0° and 760 mm. weighs 1·9766 mg., this corresponds to 4·497 mg. calcium carbonate; accordingly 0·2248 g. of the limestone is weighed out, so that each c.c. of carbon dioxide obtained corresponds to 2 per cent. of calcium carbonate in the sample.

C. SOLUTION. FUSION. EVAPORATION

In many cases the substance can be weighed directly into the vessel in which it is to be dissolved or fused; this saves time, and avoids the possibility of loss during transference from the weighing bottle to the vessel employed for the solution or fusion. It is, however, very important to select a vessel that completely fulfils its purpose, even if such direct weighing is thereby prevented.

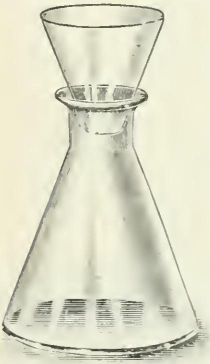
FIG. 9.

The vessels chosen should in almost all cases be adapted for heating; if this is the only consideration, beakers, porcelain basins, etc., suffice, but if there is any risk of loss from spirting, suitable precautions are necessary. The employment of very large basins or beakers as a means of avoiding loss from this cause is deceptive, and leads in other respects to both inconvenience and inaccuracy. Such operations should be carried out in narrow beakers or in Erlenmeyer flasks, which are kept covered during the process, either by clock-glasses bored through the middle, or by funnels cut off at the neck (Fig. 9), and which are subsequently washed both inside and outside with a few drops of water. Ordinary clock-glasses are not suitable, since any considerable evolution of vapour may easily raise them to one side, and thus permit a loss of liquid. The less the amount of liquid used the better, as the evaporation is thus either shortened or avoided altogether.

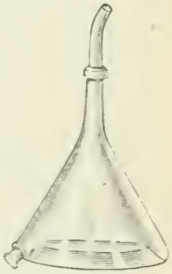
FIG. 10.

When there is not much liquid to evaporate off, the evaporation is best carried out in the vessel used for solution, especially when previous filtration is not necessary, and a precipitation, etc., is to be effected in the same vessel. With larger amounts of liquid, and especially if concentration at the boiling point is too rapid, vessels with a large surface area, such as basins, are employed, covered preferably by a funnel of the form shown in Fig. 10; or a current of air is caused to pass over the surface of the liquid by placing the basin in front of a slit leading into a chimney (Fig. 11); an adjustable glass plate is fixed over the slit in such a way that it extends beyond the basin, and a space of 1-2 cm. should be allowed between the glass plate and the basin.

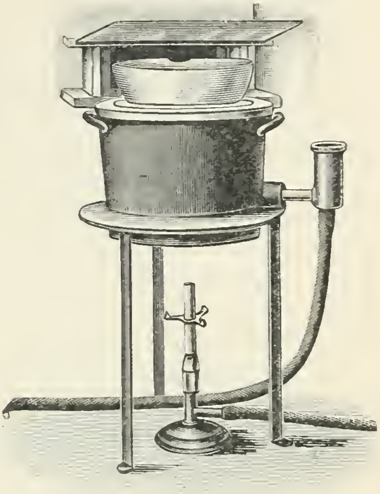
Fig. 11.

As a substitute for wire gauze and sand baths, Fritsch and Venator[1] have suggested plates of aluminium 3-4 mm. thick, heated either by a ring Fletcher burner or by a Bunsen burner, according to the size; Lunge recommends these plates as being very practical.

The question sometimes arises of avoiding contact with the sulphur dioxide and carbon dioxide formed during the combustion of the flame; this can be effected by the method of heating described below (p. 243).

D. Precipitation, Washing, and Filtration of Precipitates

Regarding precipitation, there is little to add to what is known from general analysis. In works' laboratories it is usual, and quite rightly so, not to be so scrupulous about the long standing after precipitation and before filtration as is often customary in scientific laboratories. Accurate investigations led long ago to the conclusion that even in cases where formerly it was recommended to allow a precipitate to stand twelve to twenty-four hours, quite as good results are obtained if the liquid is allowed to clear, which it does after from half an hour to two hours, and then filtered immediately. For instance, in the determination of phosphoric acid by molybdic acid, in the precipitation of sulphuric acid by barium chloride, and even in the precipitation of phosphoric acid by magnesia, etc., prolonged standing is unnecessary if definite conditions are observed; in the precipitation of sulphuric acid, for example,

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[1] *Chem. Zeit.*, 1900, **24**, 286.

the solution must be kept boiling briskly, and the chloride of barium added hot, without interrupting the boiling, in order that the precipitate may form in a granular condition. In other cases the solution must be continually stirred during precipitation; this is now much facilitated by the use of mechanical stirrers.

In scientific laboratories it is very convenient to prepare reagents in solutions of definite strength, and this is still more important in technical laboratories, as it expedites the work very greatly if it is known beforehand how much of a solution is required for a precipitation or any other reaction. It is naturally very important not to add too small an amount of the precipitant, but an excess may also be deleterious if the reagent is carried down by the precipitate, as is the case with barium chloride in presence of barium sulphate, or if the latter is soluble in an excess of the former, etc. This is avoided by the use of solutions of known strength, and by always taking the same or approximately the same weight of substance for analysis; a definite, measured volume of the reagent, sufficient for complete precipitation but not very greatly in excess, is added. In this way a single control test suffices, instead of having possibly to make a number of check tests, which always give rise to delay in stirring and allowing to settle.

In washing precipitates, a very great advantage is in most cases attainable by using almost boiling water. With proper manipulation, so that the liquids are not allowed to get cold, filtration proceeds very much more quickly than is otherwise the case, and much less wash-water is required.

By the observance of the above precautions a skilled technical chemist can effect a complete and accurate analysis of pyrites, including fusion, filtration from the residue, precipitation of the iron, of the barium sulphate, drying and igniting the residue, in from two to three hours, instead of requiring two or three days, as is often the case in scientific laboratories. To avoid the filtration and washing of a precipitate, when the filtrate only is required for further investigation, a method more frequently adopted in technical than in scientific laboratories consists in making up the liquid to a certain volume and pipetting off an aliquot part, or, as an alternative, pouring it through a dry filter paper. This plan expedites the work very much, but it is to be borne in mind that a certain error arises, owing to the volume occupied by the precipitate, which must be taken into account in accurate work, and also that in many cases more of the soluble constituents are retained, owing to "adsorption," etc., than corresponds to the interstices of the precipitate. Further, the filter paper may remove certain constituents from the liquid by adsorption; in such cases filtration must be omitted, and the clear liquid separated from the precipitate by careful decantation. If the solution is acted upon by the air, it must be pipetted directly from the graduated flask containing the precipitate. It should hardly be necessary to emphasise the importance of the pipette being carefully calibrated in relation to the measuring flask used, but errors arising from the omission of this precaution are of frequent occurrence.

The funnels selected for filtration must be of the right angle (60°), so that the filter paper can be accurately fitted, otherwise the liquid passes through too slowly; filter papers should be of close texture, and allow of rapid filtration. For analytical purposes, cut filter papers rendered ash-free by treatment with hydrochloric and hydrofluoric acids are now almost exclusively employed; pleated filter papers are not to be recommended, even for technical laboratories, on account of the very great difficulty in washing them out, except when no washing is necessary, as, *e.g.*, if the liquid has been made up to a definite volume and an aliquot part of the clear solution is to be employed for analysis.

Fig. 12.

Filter pumps are not generally used in technical laboratories except in cases in which the precipitates are particularly difficult to deal with; this is because a large number of filtrations are usually carried on simultaneously, and the various plans to avoid the tearing of the filter paper are too troublesome under these conditions. Every laboratory ought, however, to possess a filter pump, of which there are very many forms; a thick-walled "filter flask" (Fig. 12) with side tube should be used for collecting the filtrate, in order to avoid accidents due to pressure.

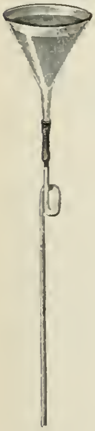

Fig. 13.

For most purposes sufficient acceleration of filtration is attained by connecting the funnel, by means of a short rubber tube, with a "fall tube," 20-25 cm. long, preferably provided with a loop (Fig. 13); this device is obviously no help unless the filter paper fits the funnel so well that the suction produced by the fall tube acts through the precipitate and no air enters from the side. Practically the same object is attained by the use of funnels with very long and fairly narrow tubes.

The Gooch crucible (Fig. 14) is now used instead of the ordinary funnel in many cases. As it has not yet been adopted in all laboratories, at least not to the extent that it deserves, some details regarding it may be useful. It is made either of porcelain or platinum, and has the bottom perforated by a number of small holes; if the precipitate has to be ignited as well as dried, as in platinum determinations, the crucible is fitted with a smooth dish-shaped tray. An asbestos filter is constructed on the perforated base of the crucible by first introducing a layer of asbestos in long fibres and then short fibre asbestos, both of which have been previously washed with concentrated hydrochloric acid and subsequently with water; a perforated plate of platinum or porcelain is placed over the asbestos, and more fine-fibre asbestos above the plate. The crucible *a* is fixed in an adapter *b* by means of a thin-walled wide rubber tube, and the neck of the adapter inserted in the neck of a filter flask *c*, to which a filter pump can be applied at *d*. Distilled water is first passed through to wash away any loose threads of asbestos, the crucible is then taken out, dried under the same conditions as are subsequently adopted with the precipitate, and weighed; the filtration is then carried out as with an ordinary funnel, the precipitate being collected on the layer of asbestos. After filtering and washing, the crucible is again placed in the drying oven, and dried at the desired temperature; if it is necessary to heat over a free flame, the supporting tray must be employed. Many estimations can be carried out successively with the same filling of asbestos, especially if the upper part of the contents of the crucible is removed without injuring the asbestos filter.

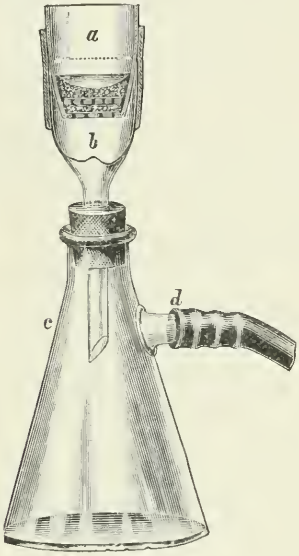

Fig. 14.

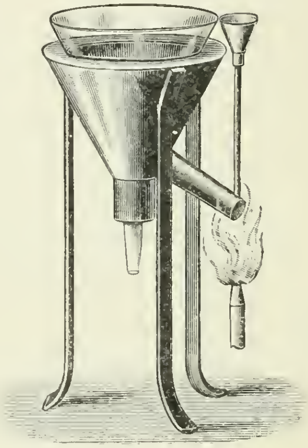
Fig. 15.

An improved form of the Gooch crucible has been described by Vollers.[1]

For filtering solutions whilst hot, the well-known hot-water funnels are mostly used. A slightly modified form, arranged for use with water, is shown in Fig. 15; the form shown in Fig. 16, consisting of a coil of

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[1] *Z. angew. Chem.*, 1905, **18**, 1272.

thick-walled copper or lead tubing, heated by a current of steam, is also very convenient.

Fig. 16.

Filtration of the precipitate is avoided by the use of centrifugation, which saves both drying and igniting, and thus leads to a great saving of time, but the method is only applicable in quite special cases. The precipitations are carried out in vessels of the form represented in Fig. 17, which have at the bottom a narrow tube closed at the lower end, on which an empirically constructed scale is etched, which shows the volume occupied by the precipitate of a definite substance for a definite unit of weight when the precipitate is reduced to the smallest possible volume by means of centrifugal force. The scale shows either the weight of the precipitate in mg., or directly the percentage of the constituent sought, when a definite amount of the original substance is employed; the precipitation is effected in the vessel itself, and the measurement is made whilst the precipitate remains in contact with the liquid.

Fig. 17.

The centrifugal method has been applied to the estimation of phosphorus, more especially in iron and steel, the precipitate of phosphomolybdic acid being measured, to the determination of urinary deposits, of cellulose in food stuffs, etc., and to a still greater extent to the estimation of fat in milk, of water in butter, and to the rapid separation of liquids containing bacilli and the like; tubes of different construction to the above are used for these latter purposes.

E. Drying and Ignition

The drying of washed precipitates in the funnel gives no trouble when a drying oven is available, but it involves some delay, which is a consideration if the result is required quickly. The time required for drying can be very considerably curtailed if the funnel is placed on a lead cone or broken beaker, and heated directly over an iron plate or wire gauze, but there is a risk of cracking the funnel in this way. It is therefore preferable, when practicable, to burn the precipitate wet in a platinum crucible, a method which is also largely employed in scientific work.

For this purpose the filter paper is carefully removed from the funnel and laid on a piece of coarse filter paper; by moving it repeatedly on to fresh dry parts of the latter and pressing very gently, the greater part of the adhering moisture can be removed in a few seconds. The precipitate and paper are then transferred directly into the crucible and ignited.

This method can be safely employed for such precipitates as barium sulphate, magnesium ammonium phosphate, calcium oxalate, silicic acid, etc.

The direct burning of the filter paper is at least as accurate as the indirect method of drying and then igniting, as the loss of substance which occurs in removing the dry precipitate with a feather or platinum spatula, and in burning the paper in a spiral of platinum wire, or on the lid of a crucible, is practically excluded; also, it has been shown that the combustion of a wet filter paper is more complete than that of a dry one, and avoids the formation of tar-like products of carbonisation.

If the external appearance of the ignited precipitate is suspicious, it is generally possible to apply an experimental check. Thus ignited barium sulphate, which is grey instead of white, should be treated with sulphuric acid, evaporated, and again ignited; similarly, if magnesium pyrophosphate shows a small dark patch, it should be treated with nitric acid (repeatedly if necessary) until the mass is pure white or greyish-white. When the precipitate is burnt wet it rarely shows anything abnormal in its condition.

If a precipitate has to be dried at 100°, 110°, or other definite temperature, it leads to great loss of time to first dry the empty filter paper, and then the paper and precipitate, till the weight is constant. The following method, which is much in vogue in technical laboratories, is preferable.

Two filter papers, as nearly as possible of the same diameter, are taken, one laid on each pan of a balance, and small pieces cut off from the heavier one until they balance each other accurately. The precipitate is then filtered on to one of the papers, dried first on filter paper, as described above, and the two filters placed in the steam oven for from one to two and a half hours, according to the nature and size of the precipitate; in weighing, the empty filter paper is placed as a tare against the one on which the precipitate has been collected.

It has been found[1] that a paper dried at 120° gains several mg. in weight if subsequently washed with alcohol and dried at 110°, as is usual in the determination of potassium; when 90 c.c. of alcohol are used for washing, the increase of weight amounts to 5 mg, which must be deducted from the weight of the potassium platinum chloride.

Rudorff[2] recommends placing the filter paper in a cylindrical weighing bottle, and drying it for thirty minutes in the drying oven, after removing the stopper of the weighing bottle; the stopper is then replaced, the bottle allowed to cool in the air for thirty minutes, and then placed in the balance case for ten minutes before weighing. After the precipitate has been transferred to the filter paper, it is similarly dried and allowed to cool before weighing.

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[1] J. Stroof, *Private communication.*

[2] *Z. angew. Chem.*, 1890, **3**, 633.

A very clean but somewhat expensive drying cupboard with removable porcelain plates is described by Treadwell.[1]

In works' laboratories ignitions are done in platinum crucibles for quantitative work; it is best to employ a solid tare in the weighing (*cf.* p. 20). The ignition of larger amounts of substance when it is unnecessary to weigh beyond centigrams, as in estimations of water, etc., can be performed in polished iron basins.

Except when a hygroscopic substance has to be dealt with, the crucible may as a rule be allowed to cool on a pipeclay triangle or on a block of marble instead of in a desiccator, and the cold crucible may be handled with clean fingers instead of with crucible tongs.

Those forms of desiccator are to be recommended which allow a free passage of air, and are accordingly provided with a calcium chloride tube, and in some cases with a soda lime tube in addition.

To clean platinum crucibles, fine sand (silver sand) is stirred up with commercial hydrochloric acid, and, after the acid has repeatedly been poured off, the crucible is gently rubbed with a portion of the moist sand; in this way the cleaning is rapidly and efficiently performed.

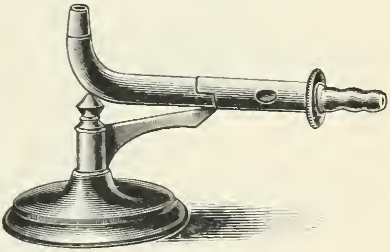

Fig. 18.

F. Heating Apparatus

Gas is the most convenient and cleanest source of heat, and when available is naturally preferable to anything else. Beyond the ordinary Bunsen burner the following more special burners are useful.

1. Burners with a horizontal bent tube (Fig. 18), known in France as the Berthelot burner. Burners of this form which turn on a hinge are also made. They are advantageous in cases where boiling over may readily occur, and where there is not sufficient height for a Bunsen burner.

2. Müncke's burner (Fig. 19) is particularly suitable as a substitute for heating in the blowpipe flame. The temperature is sufficient to melt sodium carbonate in a few minutes, so that the fusion of silicates and similar operations can be performed without a blast, and there is less risk of substance being carried away mechanically.

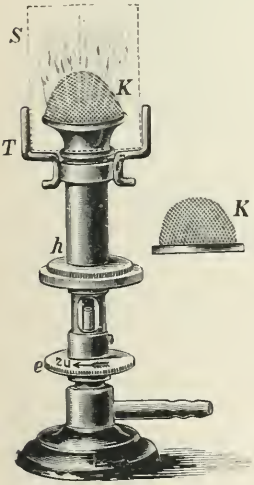

Fig. 19.

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[1] *Analytical Chemistry*, vol. ii., p. 22.

3. The Teclu burner (Fig. 20) has similar advantages to the foregoing, and by means of its various adjuncts permits of the regulation of the heat.

4. The multiple-flame burner, of which Fig. 21 shows one of the many forms, serves for heating tubes as well as for the simultaneous heating of several separate vessels. A very useful form of this burner, devised by Wiesnegg, is shown in Fig. 22, as used for heating a muffle.

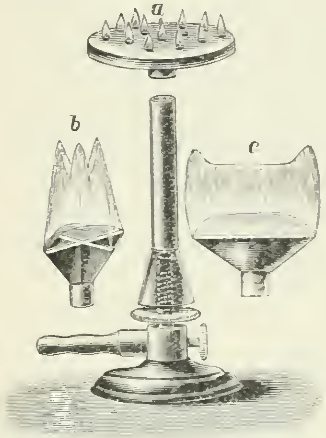

FIG. 20.

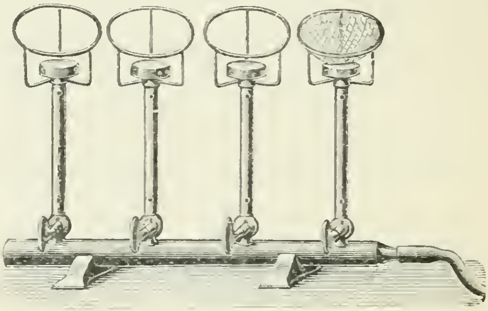

FIG. 21.

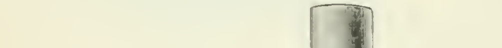

FIG. 22.

The various forms of Fletcher gas-burners serve more for general laboratory purposes than for analytical operations, and are very useful in certain technical tests. For high temperatures up to a full white heat gas ovens such as those of Perrot (Fig. 23), Seger, Rössler, and others are employed.

When heating over the naked flame is inadmissible, wire gauze or asbestos boards are used. In technical laboratories, where many vessels have to be heated simultaneously, a flat iron plate covered over with a few mm. of sand is very convenient; another and preferable arrangement consists of two pieces of sheet iron held about 5 mm. apart by rivets, thus forming a hot-air bath. Aluminium plates (p. 23) can be similarly used.

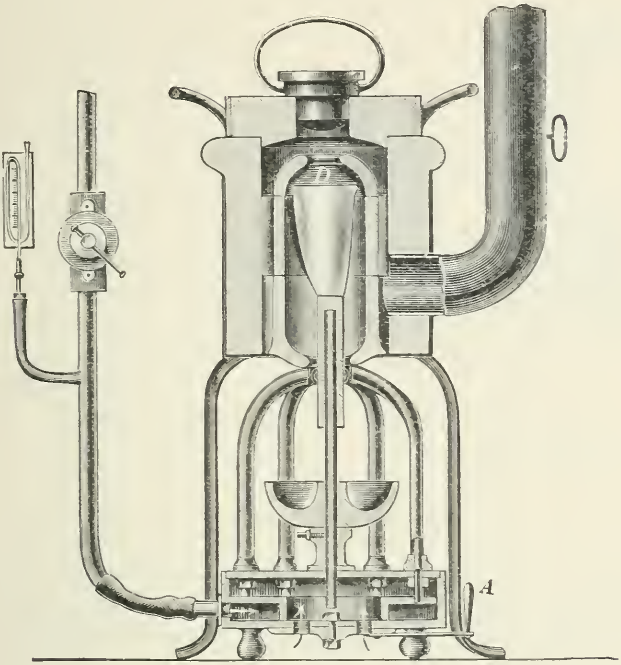

Fig. 23.

These arrangements serve for heating to temperatures from 110° to 200° or higher. For heating up to not more than 100°, a steam bath or steam-heated sand-bath can easily be fitted up in most works; the latter are particularly suitable for digesting with low boiling inflammable liquids, such as alcohol, benzene, ether, etc.

Where gas is not accessible, recourse to spirit-lamps, charcoal furnaces, etc., was formerly necessary. Now, other and more convenient heating appliances are available which give sufficiently high temperatures, such as the alcohol burner (Fig. 24), Barthel's petroleum burner (Fig. 25), etc.; petroleum tube furnaces

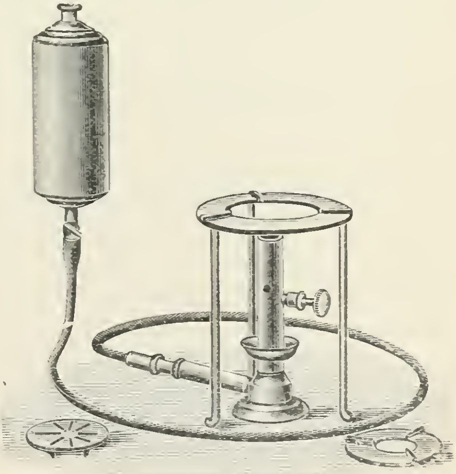

Fig. 24.

for combustions are also obtainable. These burners are free from danger, and are said to give a higher temperature than gas furnaces.

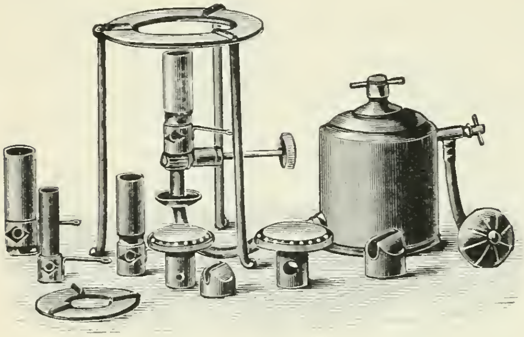

Fig. 25.

Henri St Claire Deville has designed a universal furnace (made by Wiessnegg, Paris) for use with heavy mineral oil, which serves as a muffle tube furnace or crucible furnace, and gives a temperature of 1300°.

Still higher temperatures are obtainable by means of coke furnaces and electrically heated furnaces. A description of these forms of apparatus falls beyond the scope of this section.

G. Volumetric Analysis[1]

Volumetric analysis includes "titration analysis" or volumetric analysis in the restricted sense, which consists in the application of standard solutions to the analysis of liquid and solid substances, gas-volumetric analysis, which consists in the valuation of a liquid or solid by the measurement of an evolved gas, and gas analysis. These three branches of volumetric analysis are all very extensively employed both for scientific as well as for technical work. Many of the methods are equally serviceable for both purposes, whilst others have been specially worked out for technical analysis. The latter are described in connection with the respective industries; a special section is devoted to technical gas analysis.

The Calibration and Standardisation of apparatus used in volumetric analysis.

In all branches of volumetric analysis it is of primary importance that the vessels employed should be accurately graduated, just as the first requirement for gravimetric analysis is that the balance and weights must be accurate. It has long been customary to check the weights used in analytical work, but the calibration of volumetric

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[1] The data on volumetric analysis given in this and subsequent sections comprise a number of special methods which are of technical value, and which are not usually dealt with in the ordinary text-books on quantitative analysis.

For the history of the subject, *cf.* L. L. de Koninck, *Historique de la méthode titrimétrique*, published by Havrez, Brussels, 1901; and, *Bull. de l'Assoc. Belge de Chimistes*, 1901, **15**, November and December.

apparatus is far less general; the graduations and capacity of the apparatus is too often taken on trust, especially by technical chemists.

The calibration of volumetric apparatus used in the analysis of products which are bought or sold should on no account be omitted; less accurate apparatus suffices for use in the control of working processes, but this should at least be submitted to a comparative standardisation if not actually calibrated. Apparatus for volumetric analysis can now be bought which has been tested and stamped by the National Physical Laboratory or by the Imperial Normal Standards Commission in Germany.

In the great majority of cases the apparatus tested in such institutes may be relied upon as possessing the degree of accuracy corresponding to the tests used and guaranteed by the certificate of examination. But this does not absolve the skilled chemist from the duty of taking cognisance of the character of these tests, or of himself making further tests in cases of very special importance or of doubt, just as in similar circumstances he may require to make further tests of weights adjusted by a mechanic. Also the cost incurred in the official standardisation may, in case many instruments are used, induce some to prefer doing the work themselves. This, like every other form of manipulation, requires a degree of accuracy which is obviously much greater in the hands of the officials of a standardising institute than in those of the skilled chemist, but the latter should certainly be able to do the work, and may prefer to do it in some cases. With this in view, the following details of the methods employed are given.

The conceptions as to what is to be understood by standardised vessels and what is to be required of them are very varied, and in some respects obscure. There is a considerable amount of literature on the subject[1] on which the methods and considerations that follow are chiefly based; the work of Schloesser[2] is especially important.

In the first place, the unit taken as a basis for the standardisation must be clearly defined. From the scientific standpoint the litre is the space which one kilo of water, weighed in a vacuum, occupies at its maximum density. Since this corresponds to a temperature of 4°, the work must either be always carried out at this temperature, which is naturally not practicable, or at a suitable higher temperature to be definitely determined, the corrections to be made being ascertained either by calculation or from tables. This is essential in order to ascertain the value of the "true litre" and its subdivisions, regard being had to the temperature of the water and the buoyancy of the air, which

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[1] *Cf.* J. Wagner, *Massanalytische Studien*, Leipzig, 1898; and *Z. physik. Chem.*, 1899, **28**, 193; Göckel, *Chem. Zeit.*, 1901, **25**, 1084; 1902, **26**, 159; and *Z. angew. Chem.*, 1902, **15**, 707; 1903, **16**, 49 and 562.

[2] *Z. angew. Chem.*, 1903, **16**, 953, 977, and 1904; *Chem. Zeit.*, 1905, **29**, 509.

depends on the temperature, the pressure, and the degree of moisture present. In order to avoid the calculations necessitated by the employment of the true litre, Mohr, as early as 1855, introduced as the unit the volume which 1000 g. of water occupies when weighed in air with brass weights at 14° R. = 17°·5 C. This value is called "Mohr's litre," and the designation is also extended to the use of other temperatures (15°, 20°, or higher). It is immaterial what this temperature is, so long as all utensils employed in connection with one another are standardised for the same temperature, and are subsequently used at the same or about the same temperature. In order to ensure this, the standard temperature is etched on all the utensils in question; this temperature is, therefore, the same for the vessel and for its contents (water, mercury, etc.). The "Mohr's litre" and its subdivisions were for many years in almost general use for volumetric analysis both by makers and by users of apparatus. Its convenience was then undeniably very great, since, in calibrating, all calculations which were formerly not facilitated by tables could be dispensed with.

Unfortunately, however, the desired agreement is not obtained even by calibrating at a definite temperature, since the density of the air at the time of the calibration must also be taken into account. If, for instance, we take the pressure of the air = 760 mm., and the temperature 17°·5, calculation shows that one "Mohr's litre" = 1002·3 true c.c., and one true litre = 997·7 "Mohr's" c.c. If, however, the calibration were carried out at a pressure of 700 mm., the difference due to the change in pressure would make a difference in weight of almost 0·1 g., and the volume if determined subsequently at the higher pressure would be found too small by this amount. This source of error is also not avoided by fixing a normal pressure of 760 mm. for the Mohr litre, since the buoyancy of the air depends not only on the pressure, but also on the temperature and the degree of moisture present.

Taking these considerations into account, the advantages which Mohr and his successors claimed for the choice of an alternative to the true litre disappear. The use of tables (p. 46) cannot be avoided, and the true litre in conjunction with tables (pp. 37 to 38) is, therefore, just as easily employed. It is, accordingly, very desirable that the word "litre" and its subdivisions should be restricted to the true (metric) litre, and that all chemical measuring utensils should be based upon it. At the same time it must be recognised that much apparatus standardised according to Mohr's system is still in use; the tables given below can be used to determine the deviations of such vessels from true litre measures.

The calibration of measuring flasks should always be carried out with the same kind of liquid as that with which they are to be filled when in use, so that the conditions of wetting, the meniscus correction, etc., are similar; apparatus to be used with mercury should always be calibrated with mercury, whilst burettes, pipettes, and measuring flasks are calibrated with water, which does not differ essentially in its behaviour from the very dilute volumetric solutions generally used in these vessels.

To avoid all the errors mentioned above, the only means is the employment of the true litre; as already stated, this is the volume which 1 kilo of water at 4° occupies under standard pressure. If this space is to be marked off, *e.g.* on a flask, the position of the mark will depend on the temperature of the flask. The standard temperature to which certificates are used by the National Physical Laboratory is 15° C.; thus the statement that the volume of a one-litre flask is correct means that at a temperature of 15° the volume of the contents of the flask is the same as that of a kilo of water at a temperature of 4°. The tables given below allow the adjustment to be made directly at any desired temperature and pressure, the weights that must be placed on the scale pan to effect this being given in each case.

Two true litre measures of glass, adjusted at different temperatures, differ only by the difference in the expansion of glass between the two temperatures, if water of the same temperature has been used in testing them. Therefore it is only necessary to calculate the weight which is in equilibrium with the weight of water occupying a true litre measure for one normal temperature, *e.g.*, 15°. If the temperature of the air does not greatly deviate from this, and the height of the barometer is not very far from 760 mm., mean assumptions may be made for the factors which influence the buoyancy of the air, pressure, temperature, and degree of moisture, and the reductions thus obtained may be combined with those due to the temperature of the water. The values in Table I. (p. 37) can then be employed directly in order to find how the volume of a true litre should be marked off on a flask. If, for example, the air and the water have a temperature of 17°, the empty flask along with a kilogram weight is placed on one scale pan and brought to equilibrium by a tare on the other; the kilogram weight is then removed, and on the same side (that is, along with the flask) weights to the amount of 2·208 g. are placed; equilibrium is then re-established by filling the flask with water of 17°, and the volume occupied by this weight of water marked on the neck of the flask.

In the case of greater deviations of the temperature of the air from 15°, and of the atmospheric pressure from 760 mm., Table II. (p. 38) is used to correct the values of Table I. If, *e.g.*, the height of the barometer is 720 mm., the temperature of the air 25°, that of the water 24°·3, the weight to be added for a litre is :—

From Table I.	3564 mg.
From Table II.	−92 mg.
	3472 mg.

The weight of the volume of water required to correspond to a true litre for the flask at 15° is therefore $1000 - 3{\cdot}472 = 966{\cdot}528$ g.

For any other normal temperature (t) the magnitude $(t-15)\ 0{\cdot}000027$ must be added to the above; thus for a normal temperature of 20° all the values of Table I. must be increased by $1000\ (20-15)\ 0{\cdot}000027 = 135$ mg. For a water temperature of 20°, $2699 + 135 = 2834$ mg. must therefore be added.

If a different value to the above be chosen for the mean expansion coefficient of glass, then $1000\ (a' - 0{\cdot}000027)\ (t-15)$ must be added to the values of Table I., a' denoting the new coefficient of expansion of glass, and t the temperature of the water. The amount of this correction is always very small, and is hardly likely to be employed by the chemist in calibrating.

The Tables I. and II., pp. 37 and 38, were calculated by the Normal Standards Commission, and communicated by Schloesser.[1]

The following are the methods and conditions adopted by the National Physical Laboratory for the testing and calibration of glass vessels.[2]

Vessels are calibrated either gravimetrically or volumetrically. When the highest accuracy is required, gravimetric calibration is employed. Volumetric calibration, however, which is simpler and more rapid, is in practice sufficiently exact for most purposes.

Gravimetric method.—1. *Vessels to be tested for contents.* The vessel to be calibrated is weighed empty; it is then filled with distilled water up to the mark, and weighed again, the temperature being carefully noted before and after the weighings, and the weighings reduced to weighings *in vacuo*.

The difference between the weights is the weight of water which fills the vessel at the temperature of the observation. The weight of water which would fill the vessel under the given conditions of temperature, if its volume were correct, can be calculated from a knowledge of the density of water at different temperatures, and of the expansion of the containing vessel by use of the Tables I. and II.

2. *Vessels to be tested for delivery.* The contents of the flask or other vessels are poured into a vessel of known weight, and the same procedure is adopted.

Volumetric method.—The method to be employed depends on the apparatus which it is required to test. For many purposes automatic pipettes are found useful. These are first graduated by the gravimetric

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[1] *Z. angew. Chem.*, loc. cit.

[2] The Editor is indebted to Dr R. T. Glazebrook, Director of the National Physical Laboratory, for these data. A pamphlet containing full details and charges is issued by the Laboratory.

TABLE I.

Weight in mg. to be added for 1000 c.c.; the cubic coefficient of expansion of glass = 0·000027 per 0° C. Normal temperature, 15°. Water temperature, from 5°-30°·9. Height of barometer, 760 mm. Temperature of the air, 15°. Mean pressure of aqueous vapour = 8 mg. per litre.

Temp.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9	Temp.
5	1341	1340	1339	1338	1338	1338	1338	1338	1338	1338	5
6	1338	1339	1340	1341	1342	1343	1344	1345	1346	1348	6
7	1350	1352	1354	1356	1358	1360	1363	1366	1369	1372	7
8	1376	1380	1384	1388	1392	1396	1400	1404	1408	1412	8
9	1417	1421	1426	1431	1436	1442	1447	1452	1458	1464	9
10	1471	1477	1483	1489	1496	1503	1510	1517	1524	1531	10
11	1539	1547	1555	1563	1571	1579	1587	1595	1603	1611	11
12	1619	1628	1637	1646	1655	1664	1673	1683	1693	1703	12
13	1713	1723	1733	1743	1753	1764	1775	1786	1797	1808	13
14	1819	1830	1841	1853	1865	1877	1889	1901	1913	1925	14
15	1937	1949	1962	1975	1988	2001	2014	2027	2040	2053	15
16	2066	2080	2094	2108	2122	2136	2150	2164	2178	2193	16
17	2208	2223	2238	2253	2268	2283	2298	2313	2328	2344	17
18	2360	2376	2392	2408	2424	2440	2457	2474	2491	2508	18
19	2525	2542	2559	2576	2593	2610	2627	2645	2663	2681	19
20	2699	2717	2735	2753	2771	2789	2807	2826	2845	2864	20
21	2883	2902	2921	2940	2959	2978	2998	3018	3038	3058	21
22	3078	3098	3118	3138	3158	3178	3199	3220	3241	3262	22
23	3283	3304	3325	3346	3367	3388	3410	3432	3454	3476	23
24	3498	3520	3542	3564	3586	3609	3632	3655	3678	3701	24
25	3721	3747	3770	3793	3816	3839	3862	3886	3910	3934	25
26	3958	3982	4006	4030	4054	4078	4102	4127	4152	4177	26
27	4202	4227	4252	4277	4302	4327	4352	4377	4403	4429	27
28	4455	4481	4507	4533	4559	4585	4611	4637	4663	4689	28
29	4716	4743	4770	4797	4824	4851	4878	4905	4932	4959	29
30	4987	5014	5041	5069	5097	5125	5153	5181	5210	5239	30

TABLE II.

Correction of the values in TABLE I. in mg. for 1000 c.c. for atmospheric pressure, 650-790 mm., and temperature of the air, 5°-31° C.

Mm.	650.	660.	670.	680.	690.	700.	710.	720.	730.	740.	750.	760.	770.	780.	790.	Mm.
Temp.																Temp.
5	-121	-106	- 91	- 77	- 62	- 47	- 32	- 18	- 3	+11	+26	+41	+55	+70	+84	5°
6	124	109	95	80	66	51	36	22	7	+ 7	+22	37	51	66	80	6
7	128	113	99	84	70	55	40	26	11	+ 3	+18	32	47	61	76	7
8	131	116	102	87	73	58	44	29	15	0	+14	28	43	57	72	8
9	135	120	106	91	77	62	48	33	19	- 4	+10	24	38	53	67	9
10	138	124	109	95	80	66	52	37	23	8	+ 6	20	34	49	63	10
11	-141	-127	-112	- 98	- 84	- 70	- 56	- 41	-27	-12	+ 2	+16	+30	+45	+59	11
12	145	131	116	102	88	74	60	45	31	16	- 2	+12	26	41	55	12
13	148	134	119	105	91	77	63	49	34	20	- 6	+ 8	22	36	50	13
14	152	138	123	108	94	81	67	53	38	24	-10	+ 4	18	32	46	14
15	155	141	127	112	98	85	71	57	42	28	-14	0	14	28	42	15
16	-158	-144	-130	-116	-102	- 88	- 74	- 60	-46	-32	-18	- 4	+10	+24	+38	16
17	161	147	133	120	106	92	78	64	50	36	22	- 8	+ 6	+20	34	17
18	165	151	137	123	109	95	81	67	53	39	25	-11	+ 3	+16	30	18
19	168	154	140	127	113	99	85	71	57	43	29	-15	- 1	+12	26	19
20	171	157	143	130	116	102	88	74	61	47	33	-19	- 5	+ 8	22	20
21	-174	-161	-147	-133	-119	-105	- 91	- 78	-64	-51	-37	-23	- 9	+ 4	+18	21
22	177	164	150	137	123	109	95	81	68	54	40	26	-13	+ 1	+14	22
23	181	167	154	140	126	112	98	85	71	58	44	30	16	- 3	+11	23
24	184	171	157	144	130	116	102	88	75	61	47	33	20	- 6	+ 7	24
25	187	174	160	147	133	119	105	92	78	65	51	37	24	-10	+ 3	25
26	-190	-177	-163	-150	-136	-122	-109	- 95	-82	-68	-55	-41	-28	-14	- 1	26
27	193	180	166	153	139	125	112	98	85	71	58	45	31	18	4	27
28	197	184	170	157	143	129	116	102	89	75	62	48	35	21	8	28
29	200	187	173	160	146	132	119	105	92	78	65	52	38	25	11	29
30	203	190	176	163	149	135	122	109	95	82	69	56	42	29	15	30
31	-206	193	179	166	152	138	125	112	99	86	73	60	46	33	19	31

method, and then form standards by the use of which other vessels can be calibrated.

Methods of measurement.—(i) *Flasks for contents.* In the case of flasks up to 100 c.c. inclusive, the temperature of the water is determined after the weighing; in the case of larger flasks, both before and after the weighing. If the neck of the flask is too narrow to admit the thermometer, the temperature may be taken in an auxiliary vessel. The adjustment of the meniscus is made *after* the first temperature measurement.

(ii) *Flasks for delivery.* The flask, filled to the mark, is inclined, as its contents are being poured into the tared glass, until, when the continuous stream of water has ceased, it stands nearly vertical. In this position it is allowed to drain for one minute into the glass, and the last drop is removed from it by touching against the side. The temperature is taken immediately before the adjustment of the meniscus.

(iii) *Pipettes with one mark.* The pipette is clamped vertically, and by means of a rubber tube is filled from the jet to about 1 cm. above the mark. The suction tube is closed by the finger, the water-delivery tube taken away, and the level of the meniscus adjusted to the mark. Any drops adhering to the jet are removed. The water is then allowed to run off into a tared glass, the point of the jet touching the wall of the vessel. After the continuous outflow has ceased the pipette is allowed to drain for fifteen seconds, and the jet is then stroked off the wall of the vessel. The temperature is taken on a sample collected in a special glass *before* the filling of the pipette, and on the water run out of the pipette *after* the weighing.

(iv) *Pipettes with two marks.* The method of procedure is the same as in the foregoing section, except that when the water has flowed down to within 2-3 mm. of the second mark, the suction tube is kept closed by the finger for fifteen seconds, and the adjustment to the lower mark is then made by slightly raising the finger. The last drop on the point is stroked off.

(v) *Overflow Pipettes.* These are tested like ordinary pipettes. The tap must be kept full open during the outflow. Experience has shown that accurate results can be obtained only when the pipette is filled and emptied four or five times before the actual test.

(vi) *Measuring Glasses to contain.* The glass, together with as many grams as it contains c.c., is counterpoised on the balance. The glass is removed, filled to the smallest marked volume, and then replaced. As many grams as the part to be tested contains c.c. are then taken off the balance pan, and the balance again counterpoised. After this test, the glass is filled up to the next mark and tested in the same way, and so on until the complete volume is reached. Each mark is tested from the zero. In calculating the error between two marks, if a be the error to the upper mark and b the error to the lower mark, the error between the marks is $a-b$.

(vii) *Measuring Glasses to deliver.* The measuring glass is filled up to the lowest of the divisions which it is required to test. The water is then poured into a beaker which has been counterpoised with its cover, the same regulations applying here as in the case of flasks "to deliver." After this the glass is filled to the next numbered division, and the operation repeated. The temperature is taken immediately before the first and last filling.

(viii) *Measuring Glasses with incomplete divisions.* These are usually tested at five points, viz., at the top, at the bottom, and at three intermediate points. In other respects they are treated as other measuring glasses.

(ix) *Burettes.* In all tests the water is run out continuously from the zero marks. The burette is clamped vertically, and filled up to 5-7 mm. above the zero. The water is allowed to run out exactly to the zero mark, and any drops adhering to the nozzle are removed. Care must be taken that no air bubbles are present. The tap is opened wide and the water run out into a counterpoised vessel; the flow is stopped when the water is about 5 mm. above the mark to be tested. After waiting two minutes the water is run out exactly to the mark, and the last drop touched off against the side of the glass.

Burettes fitted with glass taps should have the tap lubricated slightly with vaseline.

(x) *Gay-Lussac Burettes.* The burette is first filled as exactly as possible up to the mark. It is then inclined until the first drop flows from the outflow tube and note is taken of how far the meniscus is moved backwards. The burette is then filled to the zero, and gradually emptied into a glass counterpoised with weights corresponding to the volume to be tested, until the meniscus comes to the same point as previously. It is then placed vertically, and two minutes allowed to elapse before the exact reading is taken. Weights corresponding to the content which is being tested are then removed from the balance, and the weighing completed in the usual way.

(xi) *Measuring Pipettes.* The pipettes are clamped vertically, and fitted with a pinch-cock by means of a rubber tube. In other respects they are treated as burettes.

Amongst the general conditions specified, it is pointed out that the adjustment of the meniscus of the water to the mark of the vessel is made so that the lowest point of the meniscus is in that plane which contains the mark. In this adjustment the axis of the vessel should be vertical, and the observer's eye placed in such a position that the front and back halves of the mark coincide. A black background should be used.

Outflow jets should be drawn out straight and the ends should be smooth and even; when the tap is open full, water must run out continuously.

The limits of error are as follows, expressed in c.c. :—

(i) *Flasks.*

	For c.c.	50	100 to 250	300 to 500	500 to 1000	2000
c.c.	To contain	·05	·1	·15	·3	·5
	To deliver	·1	·2	·3	·6	1

(ii) *Pipettes.*

For c.c. inclusive	2	10	30	75	200
c.c.	·01	·02	·03	·05	·1

(iii) *Measuring glasses.*

	For c.c. inclusive	10	30	50	100	200	500	1000
c.c.	To contain	·04	·06	·1	·2	·5	1	2
	To deliver	·08	·12	·2	·4	1	2	4

For parts of the whole, less than half the total content, the limit of error is half that for the total content.

The limit of error for measuring glasses with incomplete divisions is the same as for measuring glasses with complete divisions.

(iv) *Burettes and measuring pipettes.*

For c.c. inclusive	2	10	30	50	100
c.c.	·01	·02	·03	·05	·1

For parts of the whole, less than half the total content, the limit of error is half that for the total.

Corresponding measurements of flasks for sugar determinations and for viscosity measurements are also carried out by the National Physical Laboratory.[1]

There is still much difference of opinion as regards the best method of delivery and the time interval that should be allowed. According to J. Wagner, for burettes with glass stopcocks, a total time of outflow of 70 seconds is sufficient, and in the case of burettes with clips, 45 seconds; it would be preferable to say that burettes should empty in 40-75 seconds, according to the size. Pipettes can be emptied much more accurately than the official instructions assume; an accurate although somewhat tedious method consists in making a determination between two marks on the pipette, and sufficient accuracy is attained also by blowing out. As Göckel rightly points out, it is very wearisome to have to wait 2 minutes with measuring pipettes, and it would be better to prescribe an interval of $\frac{1}{4}$ minute. Ostwald prefers blowing out; others, touching against the wall of the vessel.

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[1] *Note.*—The conditions of official standardisation adopted in Germany are given in the German edition, vol. **1**, pp. 47-50. They are also described by Weinstein, *Z. angew. Chem.*, 1904, **17**, 1745. *Cf.* also *Fischer's Jahresber.*, 1897, **43**, 1146; and Schloesser, *Z. angew. Chem.*, 1903, **16**, 977.

According to Schloesser, the method of delivery, whether free or against the wall of the receiving vessel, is immaterial; the differences arising therefrom are small. Free delivery with subsequent removal of the drop seems preferable, however, in the case of burettes, because the end reaction can be then more readily recognised; this applies also to pipettes, because there is then no temptation to hold them obliquely, which is always objectionable. Blowing out, on the other hand, Schloesser absolutely rejects, an opinion in which Lunge concurs, since it gives rise to too great differences between different observers. As regards the time interval to be allowed for delivery, it is only necessary to wait until the residual liquid has been reduced to a negligible small amount; in the case of pipettes, this can be taken as $\frac{1}{4}$ minute.

Should it be desirable for some special reason to undertake the calibration of apparatus, this can be done with sufficient accuracy, and within the official limits of error, by employing a sufficiently stable balance, turning with 0·05 g., for vessels holding up to 500 c.c., and an ordinary analytical balance and a weighing bottle, provided with a glass stopper, for smaller vessels. The temperature of the water employed in calibrating should be determined with an accurate thermometer to within ± 0·1°.

The contents of ordinary pipettes are emptied at one delivery into the weighing bottle, those of burettes and measuring pipettes in portions of 2-10 c.c. at a time, according to the accuracy desired; the conditions with regard to the holding of the pipette, removal of the drop and the interval allowed for draining as practised at the National Physical Laboratory being observed. If Mohr's system is used, the weight for the normal temperature chosen must be calculated according to the Table on p. 46. For the true litre the data given on p. 35 *et seq.* are to be observed, and Tables I. and II. (pp. 37 and 38) used for the necessary corrections. The error of the vessel is then given by the difference between the calculated additional weight and that actually required.

If the vessel is calibrated for delivery, thorough cleaning must be strictly attended to (*cf.* p. 50).

At least two calibrations should be made, and more if there are large differences in the determinations, and from the mean of the results a table of corrections is drawn up. In the case of measuring flasks and ordinary pipettes, it is preferable to alter the graduation to the corrected position.

If a great many calibrations have to be carried out the delay due to weighing may be avoided by the use of standard measuring instruments, although this is less accurate than direct weighing. For this purpose the Ostwald pipette (Fig. 26) is usually employed. These pipettes are made to hold 2 or 5 c.c., according to the degree of accuracy required, and are tested as follows. The pipette is fitted on to the lower end of the burette, as shown, the burette is filled with water of the normal temperature, and then by opening a pinch-cock at *a* the pipette is filled exactly up to the mark *b*. A weighing bottle is then placed below the pipette, the pinch-cock at *d* opened, and the water allowed to flow out until it just reaches the mark *c*, one or preferably two minutes being allowed to elapse for completion of the delivery. It is unnecessary to connect the side tube of the pipette with the jet of the burette, instead of, as is shown here, with the rubber tubing, if this 1-2 minutes' interval is allowed. The mean of three weighings of the contents of the pipette, if they agree well among themselves, is taken as the standard. To calibrate the burette *e*, it is filled with water at any desired temperature, which, however, must remain constant during the calibration; then, by opening *a*, the water is allowed to rise to *c*, and the burette filled to the zero mark. By again opening *a*, the water is allowed to rise exactly to *b*, and a reading of the burette taken. The water in the pipette is next allowed to run out to *c* by opening *d*, and the pipette again filled up to the mark *b* by opening *a*; the position in the burette is again read off, and so on until the burette is empty. An interval of a minute is allowed to elapse before each reading in *e*, *b*, or *c*. The mean of two series of experiments is taken, and the actual capacity of each interval of the burette, corresponding to the capacity of the pipette, is thus determined. If, for example, the capacity of the pipette determined by the use of Table I. has been found to be 2·1234 true c.c., and if the first pipette delivery occupies 2·20 c.c. in the burette, each c.c. of the burette $= \frac{2\cdot20}{2\cdot1234} = 1\cdot036$ c.c. If the reading of the burette after the second delivery is 4·35 c.c., each c.c. in this section contains $\frac{4\cdot35 - 2\cdot20}{2\cdot1234} = 1\cdot013$ c.c., and so on. In this way a correction table for the burette readings can be constructed.

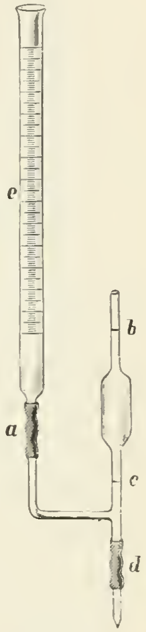

Fig. 26.

Cushman[1] mentions an improvement on the Ostwald pipette which Ostwald himself had previously adopted, which consists in graduating the upper narrow tube, care being taken that the capacity of the pipette from the mark *c* to about the middle of the upper tube *b* is 2 c.c. It is then not necessary to determine the capacity of the pipette by a number of accurate weighings as above, but only to find the value of the pipette scale with regard to the burette scale by a few determinations. In calibrating, 2 c.c. at a time are allowed to pass from the

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[1] *Chem. News*, 1902, **85**, 77.

burette into the pipette, and the height of the liquid in the latter noted; the corrections of the burette can thus be calculated. This calibration is of course only relative; if the absolute values of the graduations are required, the capacity of the pipette must be determined in the ordinary way. Or it may be found by making a few weighings, so as to ascertain up to which of the graduations on the upper tube the pipette has to be filled so that it holds exactly 2 c.c.; it is subsequently always filled up to this mark, and used for calibrating according to the method described above, whereby the corrections to be applied to the readings of the burette can be found without much calculation. For calibrations according to the true litre, attention must be paid to the details on p. 35 *et seq.*

In the calibration of measuring instruments for gases, a distinction must be drawn between apparatus for the actual analysis of gases, for which only relative measurements are required, and that employed for gas-volumetric analysis, *i.e.*, the estimation of a constituent of a solid or liquid in the gaseous form, for which purpose absolute measurements are necessary. A further distinction must be made, according as whether the gas is confined over water, over mercury, or in the use of nitrometers, over sulphuric acid, and the meniscus correction for the confining liquid must be allowed for, in case measurements are made at parts of the tube of unequal bore. Lastly, instruments must not be calibrated in an inverted position compared with that in which they are to be employed, since the menisci will then be inverted; or if this is unavoidable, the necessary meniscus correction must be ascertained.

The expansion of the glass is, in these cases, scarcely ever taken into account. The temperatures of calibration should be stated as in the case of liquids, $\frac{15^\circ}{4^\circ}$ or $\frac{20^\circ}{4^\circ}$, etc., since if the calibration has been effected at 15°, determinations made at this temperature and at 25° are not equivalent.

Göckel points out that the plan of taking the mean of the readings at the highest and lowest points of the meniscus, as the correct reading, is decidedly to be condemned. L. W. Winkler[1] regards the values for the meniscus correction given by Bunsen[2] as too low; according to more recent determinations by Göckel,[3] however, Bunsen's figures are very near the correct values. As these corrections are not required for ordinary volumetric apparatus, reference to the original papers will suffice.

The time interval of two minutes before taking a reading, as recommended in the case of burettes, is not applicable to gas measuring tubes,

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[1] *Z. anal. Chem.*, 1901, **40**, 403; and *Z. angew. Chem.*, 1903, **16**, 718.

[2] *Gasometrische Methoden*, 2nd edition, p. 38.

[3] *Z. angew. Chem.*, 1903, **16**, 49.

since it depends on their form and diameter. In most cases, the values given below for the time taken by the water, used in gas burettes, to attain its final position may be taken as correct.

For	25 c.c.	3 minutes.	For	125 c.c.	7 minutes.
,,	50 ,,	4 ,,	,,	150 ,,	8 ,,
,,	75 ,,	5 ,,	,,	175 ,,	9 ,,
,,	100 ,,	6 ,,	,,	200 ,,	10 ,,

The capacity of gas burettes graduated to hold exactly 100 c.c., or any other definite volume between two glass stopcocks, such as Winkler's burette, is hardly ever correct, and the actual capacity should always be determined and the corrected value marked on the burette; it should further be noted for which point of the meniscus the reading has been calibrated, and whether the meniscus correction has been made for water or for mercury.

Gas measuring tubes graduated in mm., such as the Bunsen eudiometer, can of course be used at any temperature and with any confining liquid; they must be specially calibrated in each case, and a corresponding table of corrections drawn up. Such measuring tubes are scarcely ever used in technical analysis.

The temperature of the volumetric solutions should really be always the same as that at which the burette was calibrated, and this temperature should be indicated on the vessels (*e.g.*, $\frac{15^\circ}{4^\circ}$, $\frac{17^\circ\cdot5}{17^\circ\cdot5}$, etc.) From this point of view some prefer the calibration to be made at 17°·5 or 20°, because these temperatures approximate more to the average laboratory temperature. Small deviations from the normal temperature can be overlooked, as their effect falls within the limits of experimental error, but a considerable error is introduced by working at a temperature of say 8° to 10° or even lower, as often happens in works' laboratories in winter, or, on the other hand, when the temperature rises to 25° or more in summer, as may occur in the best laboratories. Under such circumstances if the temperature differs from the normal by more than 2°, the necessary corrections are imperative. In most cases these corrections may be made with sufficient accuracy on the basis of the expansion of distilled water; if greater accuracy is required, the tables drawn up by A. Schulze[1] for a number of normal solutions may be used. For correcting readings when the temperature of the water exceeds 15°, use may be made of the following table, calculated by Schloesser[2] for the expansion coefficient of glass = 0·000027, and the values for the expansion of water given by the Physico-technical Reichsanstalt. The figures given in the table are the number of c.c. which must be subtracted from 1000 c.c. to give the volume of

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[1] *Z. anal. Chem.*, 1882, 21, 167.

[2] Private communication.

distilled water which at t° fills a litre flask, calibrated at 15°, so that it occupies a volume of 1000 c.c. at 15°.

Temp.	c.c.	Temp.	c.c.
15°	0·000	23°	1·348
16°	0·130	24°	1·563
17	0·272	25°	1·788
18°	0·42	26°	2·023
19°	0·58	27°	2·267
20°	0·76	28°	2·520
21°	0·94	29°	2·782
22°	1·14	30°	3·053

This table holds for the apparent expansion of distilled water. The values for *N*/5 and *N*/10 solutions differ so slightly from these, that the table may also be used for these solutions. For *N*/1 solutions, on the other hand, the deviations are greater: for hydrochloric acid, the expansion between 15° and 25° may be taken as 2·42 per cent.; for oxalic acid, 2·62 per cent.; for sulphuric acid, 3·05 per cent.; for sodium hydroxide, 3·15 per cent., and for sodium carbonate, 3·03 per cent.

In using such solutions errors may also be introduced by working at temperatures differing appreciably from that at which the solutions were standardised. For instance, in the case of normal hydrochloric acid, standardised at 15°, readings made at 10° must be divided by 0·9991 and readings at 20° by 1·0011, in order to avoid an error of ± 0·1 per cent.; for normal sulphuric acid the error is about 1½ times greater than for distilled water.

APPARATUS FOR VOLUMETRIC ANALYSIS

The ordinary apparatus used in volumetric analysis, such as measuring flasks, measuring cylinders, pipettes and burettes, is familiar to every technical chemist, and is fully described in text-books on analytical chemistry. Attention may, however, be advantageously directed to some points of particular importance for technical laboratory work.

Burettes.

The cheapest and most convenient of the various forms of burette is that shown in Fig. 27, in which the exit tube is closed with a glass bead, thus dispensing with a metal pinch-cock.

By squeezing the rubber tube outside the bead *a*, it takes the form shown in Fig. 28, thus leaving a space at each side through which the liquid flows out; with a little practice in the manipulation, the liquid can be allowed to escape as quickly or as slowly as may be desired. This arrangement lasts much longer than any of the various forms of pinch-cock, with their accompanying rubber tubes, and can even be used in gas analysis apparatus such as the Orsat apparatus, in place of expensive and fragile stopcocks.

Burettes with glass stopcocks are, however, indispensable for potassium permanganate and iodine solutions; those with stopcocks at the side should be employed.

When used in the control work of manufacturing processes, no special precautions in reading burettes are necessary. For more accurate laboratory work, however, the following precautions are necessary:—

In order to be fairly certain of reading burettes of 50 c.c. capacity, and graduated in $\frac{1}{10}$ c.c. to within 0·01 c.c., the use of a pocket lens is advantageous; it is also necessary to avoid two sources of uncertainty, namely, the indistinct boundary between air and liquid, and the parallax error. The first is generally avoided by taking the lower boundary line of the black meniscus as the normal reading, but this cannot be done in the case of dark liquids such as permanganate solution. The boundary line is rendered much sharper by shutting off the light from below, by holding a sheet of black paper behind the burette, with the upper edge some mm. below the meniscus; as an alternative, the fingers held close together may be used. It is scarcely necessary to illuminate the upper part specially. Instead of black paper, G. Bergmann[1] proposed the use of a blackened wooden clamp with a holder, which is fixed on to the burette from the side, and on which a milk-glass plate is screwed. Schellbach recommends the use of burettes with two narrow white longitudinal strips at the back; in this way a fine point, which can easily be read, is formed at the boundary of the meniscus.

FIG. 28.

The use of floats naturally obviates the difficulty arising from the want of definiteness of the meniscus, provided that they are accurately made and that their mark is finely etched.

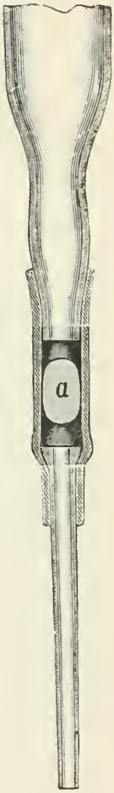

FIG. 27.

The second source of uncertainty is due to parallax. If the eye is not quite accurately in the plane of the meniscus, the reading may be several hundredths of a c.c. either too high or too low. This is obviated by having a circular mark for reading, which appears as a single line when the eye is exactly in its plane. For this purpose Erdmann devised the cylindrical float, which is, however, open to the objections that it often sticks, especially when the burette is being filled, and that the greater accuracy of reading hoped for from its use is rendered quite illusory by its frequently taking an oblique position and by the unequal capillary rise of the liquid between its exterior wall and the inside wall of the burette. For these reasons most chemists have abandoned its use.

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[1] *Z. angew. Chem.*, 1898, **11**, 853.

The spherical float of Beutell (Fig. 29), in which capillary effects are obviated, is a considerable improvement on that of Erdmann. With a good float of this kind, one which takes a true vertical position, an experienced observer can read quite well to 0·01 c.c. and in any case with much greater certainty than without a float, when ordinary burettes without circular marks are used.[1] These floats are often not properly weighted, and consequently hang obliquely; they are then quite useless.

To take readings to 0·01 c.c. with a float, it is preferable to use a magnifying glass, or for greater certainty, a reading telescope; but the increased accuracy thus obtained is illusory if the errors of the burette are too large, or if the graduations are too coarse or not sufficiently uniform, as is often enough the case. The graduation of Erdmann's float in ninths, as proposed by Prinzl, although in principle undoubtedly an improvement, has scarcely come into use, chiefly because it can only be employed for cylindrical floats, the drawbacks of which have been mentioned above.

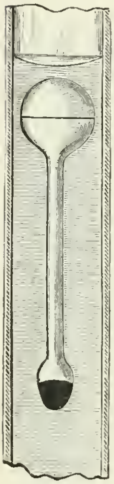

Fig. 29.

The utility of using floats has been much disputed, *e.g.*, by Reinitzer, Andrews, J. Wagner, Kreitling, and Schloesser. The majority of the objections raised, however, apply to the cylindrical Erdmann float, and include the points referred to above. Lunge regards a properly constructed Beutell float as reliable and satisfactory.

Ordinary floats cannot be used for fairly strong permanganate solution, on account of its dark colour. The double spherical float proposed by Rey,[2] one sphere of which projects above the liquid and carries the mark, for such solutions, is unsatisfactory, on account of the difficulty of getting floats of this kind which hang vertically and also because the upper sphere is too small. The floats constructed by Diethelm[3] are somewhat better, but the upper bulb is also unavoidably too small.

Many chemists are prejudiced against the use of floats altogether, because they are often faulty in construction and wrongly used. The German Imperial Normal Standards Commission also condemns them and desires to replace them by having the graduations carried either right round, or three-fifths or half-way round the burette; the burette must then be placed so that the graduations are on the left-hand side of the observer, are visible both from the back and front, and appear as a single line at the point of reading when the head is held in the proper position. In this way parallax is certainly avoided, but the

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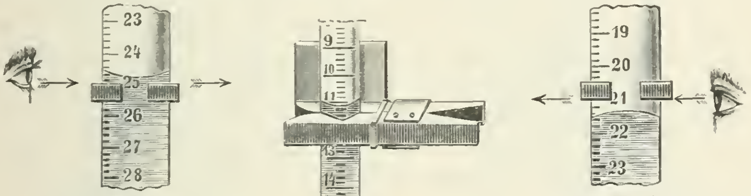
[1] *Cf.* G. Lunge, 5*th Congress of Applied Chemistry*, 1903.

[2] *Ber.*, 1891, **24**, 2098.

[3] *Chem. Zeit.*, 102, **26**, 607.

uncertainty in the reading of the meniscus remains, and must be overcome by the use of an illuminator; also, such burettes are expensive (about 1s. 6d. to 2s. dearer than ordinary burettes of the same accuracy), and, according to the makers, they are more fragile than those with short graduations. The objection has been made that these longer graduations are fatiguing to the eye, but this, and also their greater fragility, are denied by Schloesser.

The problem of avoiding parallax and at the same time attaining a sharper reading is, according to Lunge, most satisfactorily solved by the use of the light screen constructed by Göckel[1] (Fig. 30), which renders both floats and circular graduations unnecessary. It is based on a principle similar to that of Bergmann's clamps (p. 47), and, like these, is clamped on the burette 2-3 mm. below the lowest point of the meniscus; owing to its diagonal form, it can be fitted to tubes of from 9-20 cm. diameter with one and the same clamp. The black clamp shades off the superfluous light, thus forming a very sharp, dark boundary line. If necessary, especially when the light is not very good, a sheet of white paper may be held behind the burette to give better illumination on the scale, or it may be fixed to the clamp, thus acting as a complete substitute for the fragile frosted-glass plate employed by Bergmann. The new feature in Göckel's screen is the avoidance of parallax, by making the opening of the screen exactly at right angles to its horizontal surfaces. Small metallic plates, screwed to the clamp, act in such a way that on opening and closing the screen its motion is always in the same plane. In order to avoid parallax, therefore, it is only necessary to bring the eye into such a position that the front and back edges of the upper surface of the screen coincide. The same object can be attained for a mercury meniscus by placing the screen 2-3 mm. *above* it, as shown in the figure.



H_2O Meniscus

Hg. Meniscus

FIG. 30.

Lunge[2] regards Göckel's screen as thoroughly satisfactory, and is of opinion that it makes the use of floats in ordinary burettes with short graduations quite unnecessary; it may also be employed for avoiding parallax in dealing with opaque solutions, such as permanganate, although in such cases the meniscus is, of course, invisible.

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[1] *Chem. Zeit.*, 1903, **27**, 1036.

[2] *Z. angew. Chem.*, 1904, **17**, 198.

Dupré[1] uses a small glass rectangular mirror, 72 by 50 mm., for reading burettes. The lower portion of the mirror is covered with a piece of paper, fixed parallel to the side of the mirror, the right-hand half of the paper being white and the left-hand half black. In taking a reading the mirror is held against the back of the burette in such a position that the black part of the paper gives the best definition of the meniscus, and the head is so placed that the pupil of the eye is seen reflected at the same height as and close to the division to be read.

Before being used, burettes, pipettes, and other measuring vessels must be well cleaned, especially from fatty substances. The following reagents are recommended for this purpose:—alcohol and ether; strong sodium hydroxide solution, followed by water, hydrochloric acid, and then water again; strong nitric acid; acidified permanganate solution for from one to two days. A mixture of sulphuric acid and potassium bichromate is probably the most useful reagent; it can be kept for several months, and in obstinate cases may be used warm.

The German Imperial Normal Standards Commission (1902) rightly condemns the use of hydrofluoric acid for cleansing purposes, as is sometimes recommended, and also the use of all other strongly acting chemicals, which is going somewhat too far. They give the preference to soap and water (concentrated and hot if necessary) to be applied either with strong brushes, or by shaking with filter paper, according to the shape of the vessel. Such mechanical cleaning is certainly preferable to any other method.[2]

Insufficiently cleaned burettes, etc., give rise to serious errors by the adherence of drops to the dirty parts; instruments, which in spite of all efforts cannot be satisfactorily cleaned, should only be used for rough estimations.

Different liquids wet glass to a different extent, and consequently give different volumes on delivery. According to J. Wagner (*cf.* p. 41), who has made experiments on this point, the errors arising in this way are, as a rule, negligible, but in the case of concentrated sulphuric acid the amount adhering to the glass is much greater than in the case of aqueous liquids (0·7 per cent. instead of 0·2 per cent.), and this must be taken into account in the analysis of nitrous vitriol.

In technical laboratories, none of the more complicated forms of burette stands and holders should be used, but only the simplest and cheapest, more particularly those which hold a large number of burettes. It is very necessary to choose forms in which no part of the scale is covered by the holder. A very simple and inexpensive form is shown in Fig. 31.[3] The burette fits into the semicircular opening in the wooden support, and is held against it by the piece of gut *a* attached to the peg

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[1] Private communication to Prof. Lunge.

[2] *Cf.* Schloesser, *Z. angew. Chem.*, 1903, **16**, 962.

[3] Made by C. Desaga, Heidelberg.

b; by turning *b*, *a* can be loosened, so that the burette can easily be taken out or replaced.

Burettes are very largely employed in technical laboratories, which have an arrangement for filling them from below by means of a side tube, or by means of a T-piece introduced between the lower end of an ordinary burette and the delivery tube; a rubber tube is joined to the horizontal arm of the T-piece and leads to a stock-bottle at a higher level (Fig. 32). The burette is filled from below, a pinch-cock or glass stopcock being attached to the side tube to regulate the supply of the solution; an obvious saving of time and gain in cleanliness is thus effected. This method of filling has also been suggested for liquids which must not be brought in contact with rubber;[1] this may be done by making a rigid glass connection between the burette and the stock-bottle, sealed on to the burette at its lower end, and with the upper end dipping into the bottle, like a syphon. This arrangement is, however, much too fragile, as it may be easily damaged by shaking. It is

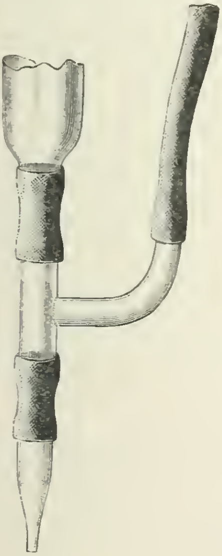

FIG. 32.

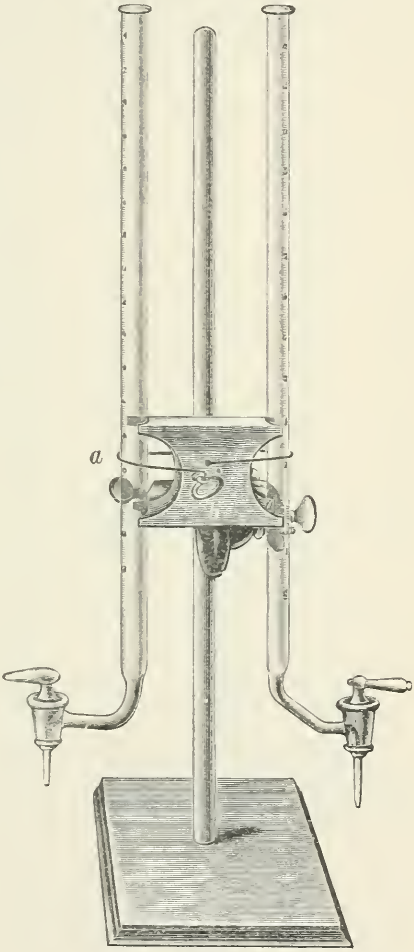

FIG. 31.

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[1] Gawalowski, *Z. anal. Chem.*, 1885, **24**, 218.

important to bear in mind that whether burettes are filled from an attached stock-bottle or by hand, it is always necessary to shake the stock-bottles of normal solutions at least once a day, preferably at the beginning of the day's work, in order to mix the water which has evaporated and condensed on the upper empty part of the bottle with the rest of the solution; such shaking is obviously out of the question with a rigid connection, such as that suggested above. Stock-bottles, if connected for filling up the burette as described above, must be shut off from the air by tubes containing calcium chloride, caustic alkali, etc., or, less conveniently, a tube may be led from the stock-bottle into the top of the burette, so as to prevent changes by evaporation of water, absorption of carbon dioxide, oxygen, etc. The large stock-bottles in which the volumetric solutions are kept in bulk, and which often are of a capacity of 50 litres or more, must be similarly shaken before filling the smaller supply-bottles; this is facilitated by making use of the ordinary stands for carboys.

The apparatus constructed by O. Knöfler, in which the burette is fixed into the stock-bottle itself, and filled from below by blowing in air with a rubber ball, is very convenient for many purposes. Various forms of this apparatus are obtainable. Contact with rubber can be avoided by this device without making it impossible to shake the bottle.

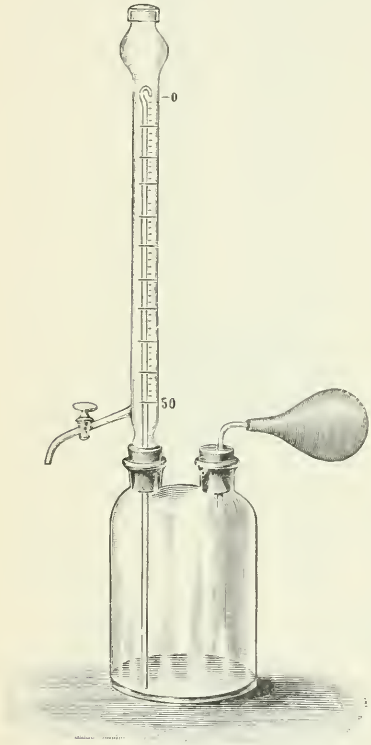

Fig. 33.

An overflow arrangement can readily be connected to burettes of this type, as shown in Fig. 33; in this case it is not necessary to adjust to zero, because this is regulated by the upper end of the burette itself, since the liquid which overflows, when filling, runs back into the bottle.

Göckel[1] has devised a burette with a long bent side tube for titrating hot solutions; an apparatus for facilitating the titration of a large number of solutions has been constructed by W. Schmidt.[2]

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[1] *Z. für chem. Apparatenkunde*, 1905, 1, 99.

[2] *Chem. Zeit.*, 1904, 28, 154.

Pipettes.

Graduated pipettes of large dimensions are seldom required; the most useful sizes are 1 c.c. (divided in $\frac{1}{100}$ths), 2 c.c. (divided in $\frac{1}{50}$ths), and 5 c.c. or 10 c.c. (divided in $\frac{1}{20}$ths or $\frac{1}{10}$ths). Since they are mostly used for measuring out the solutions to be analysed, great stress must be laid on their accuracy. The method of delivery has been described above (p. 39).

The measuring vessels suggested by O. Bleier,[1] of which the measuring pipette is shown in Fig. 34, are designed to deliver quantities up to say 50 c.c. by means of one and the same pipette, according as the point *b*, *c*, *d*, *e*, or *f* is taken as zero. The capacity from *b* to *c*, *c* to *d*, *d* to *e*, and *e* to *f*, must always be exactly 10 c.c., and the connecting tubes must not be too wide, as otherwise the practical value of the device is lost.

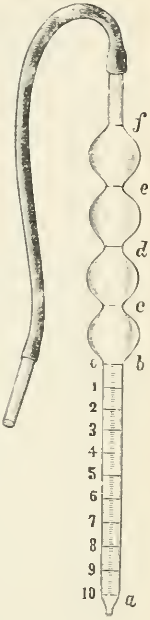

FIG. 34.

As regards the method of using ordinary pipettes, reference may be made to p. 42. Pipettes which have the graduation on the upper part only, and which accordingly deliver their full content, are preferably used only for less important work, such as in the control of a manufacturing process; when the greatest possible accuracy in measuring is desirable, it is preferable to use pipettes having a lower graduation as well. The latter should be just above the contracted part of the tube, at the point to which the pipette empties itself when used for dilute solutions. The tediousness referred to by J. Wagner in using a pipette with two marks is then avoided, even when the necessary interval for draining is allowed, which is best done as follows. The pipette is run out to within a few mm. above the lower mark, an interval of $\frac{1}{4}$ minute allowed, then run out accurately to the mark, and finally the last drop removed. Before adjusting to the upper mark, the liquid wetting the lower part of the pipette on the outside should always be washed off with water.

When one and the same volume of liquid has often to be measured off, self-adjusting pipettes (overflow pipettes) are very suitable, especially when large amounts (50-100 c.c.) have to be taken. There are many forms of these pipettes, of which those shown in Figs. 35 and 36 are examples.

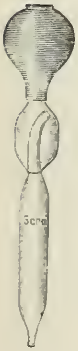

FIG. 35.

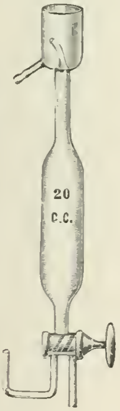

FIG. 36.

It must not be overlooked that, even under the most favourable circumstances, measuring in pipettes is far less accurate than weighing. The procedure very

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[1] *Chem. Zeit.*, 1897, **21**, 1028.

generally and advantageously adopted for technical work, of weighing out a large amount of substance, dissolving it in a measuring flask and withdrawing an aliquot part of the solution for analysis, is never as accurate an analytical operation as the weighing out and direct analysis of a small amount of substance, even if the measuring vessels have been carefully calibrated. The advantages of the latter method may, however, be more than counterbalanced by the difficulty of obtaining a satisfactory average sample in small bulk.

Vessels used for Titration.

Beakers are employed as a rule, but if it is desirable to exclude air as much as possible, ordinary or Erlenmeyer flasks are preferable; a current of carbon dioxide can be passed into the flask during the titration, if desirable. Dupré[1] uses a large bulb U-tube; when the colour change of the indicator in use appears, in the portion of the solution contained in the bulb into which the titrating solution is delivered, the contents of the tube are mixed by gentle shaking. The titrations are thus carried out rapidly and with safety.

Quality of the Glass employed in volumetric analysis.

Attention to the quality of the glass of which the measuring vessels, beakers and flasks, employed in volumetric work, are made, is of importance. It has long been known that many kinds of glass are gradually attacked even by distilled water, and more readily by alkalis, with the liberation of both silicic acid and of alkali. Glass is much more resistant towards acids. Formerly, it often happened that burettes in which sodium hydroxide had stood for a long time developed cracks, but this seems to be of less frequent occurrence now; dependence should, however, not be placed on standard alkaline solutions which have stood for a long time in vessels made of ordinary glass, without further standardisation.

Glass is attacked to a much greater extent on heating. For this reason, the sharper change of colour shown by phenolphthalein and litmus as compared with methyl orange is, in many cases, quite deceptive, because, when the first two indicators are used, long boiling is necessary to drive out the carbon dioxide, and if this is done in vessels made of ordinary glass, the amount of alkali may easily come out distinctly too high. This can be guarded against by using porcelain vessels, or, though by no means perfectly, by using specially made glass, such as Jena "resistance glass."

That glass giving a strongly alkaline reaction is still sometimes met with in commerce, has been pointed out by C. Liebermann.[2]

Lunge[3] states that on boiling normal sodium carbonate solutions in

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[1] Private communication to Prof. Lunge.

[2] *Ber.*, 1898, **31**, 1818.

[3] *Z. angew. Chem.*, 1904, **17**, 196.

vessels of ordinary Thuringian glass, for a long time, considerable amounts of sodium and of silicic acid go into solution, calcium silicate being precipitated, and that even Jena resistance glass is distinctly acted upon under the same conditions.

INDICATORS FOR ACIDIMETRY AND ALKALIMETRY[1]

Acidimetry and alkalimetry depend on the fact that when acid and alkaline solutions, which, however, need not necessarily contain free acids or alkalis, are brought together, a definite point is reached at which the indicator, which has been added to one of the solutions, changes colour.

A very great number of indicators have been suggested, but the majority have been found to be of but little value in practice; many of them are quite useless for accurate work, and most of them are superfluous. Only three indicators, which suffice for all purposes, are in general use—*litmus*, *methyl orange*, and *phenolphthalein*. In fact, litmus, although the oldest indicator, and formerly almost exclusively used, can also be dispensed with, and is now only used in many laboratories in the form of litmus paper; but all eyes are not so sensitive for the change of colour with methyl orange as with litmus, and for this reason, as also from long custom, litmus is still widely used.

Indicators are usually divided into three classes—(1) those which are only slightly or not at all sensitive to weak acids, such as carbonic acid, sulphuretted hydrogen, silicic acid, boric acid; (2) those of medium sensitiveness; (3) those which are almost as sensitive to the weakest as to the strongest acids. Indicators of the first class have a distinctly acid character; they combine with all bases, even weak ones, to form salts, which have a definite colour and which are only decomposed by stronger acids, with the production of a different colour pertaining to the free acid. They are therefore sensitive to alkalis and to strong acids, but not to weak acids. The most important of these is methyl orange; other azo-colouring matters such as tropäolin OO, Congo red, and benzopurpurin are also used, and further, lacmoid, cochineal, para-nitrophenol, and iodoeosin, the latter being particularly sensitive towards alkalis.

The third class has exceedingly weak acid characters, usually only phenolic, and their salts are therefore decomposed even by the weakest acids. These indicators are very sensitive to acids, even carbonic acid and sulphuretted hydrogen, less sensitive to bases. The most important indicator of this class is phenolphthalein; others are, turmeric, rosolic acid, flavescin, etc.

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[1] A comprehensive account of indicators and their applications is given in the following monographs:—A. I. Cohn, *Indicators and Test Papers*, 2nd edition, 1902; F. Glaser, *Indikatoren der Acidimetrie und Alkalimetrie*, 1901.

The second class forms the transition between the other two; it includes indicators which are somewhat sensitive even to weak acids, but less so than those of the third class, and for this reason there are often gradual transitions when using them, in titrating, which do not coincide with the formation of definite compounds. If the weak acids set free during titration, such as carbonic acid and sulphuretted hydrogen, are removed by boiling, they act like the first class. Litmus is the chief representative of this class; others are phenacetolin, alizarin, hæmatoxylin, etc.

Since strong acids, such as hydrochloric acid or sulphuric acid (oxalic acid has almost gone out of use in alkalimetry), and strong bases are now universally used as normal solutions, the following conclusions regarding the use of indicators may be accepted.

The *strong mineral acids* can be titrated sharply with all indicators, but most reliably and, in the cold, only with those of the first class; with the third and even with the second class, the normal alkalis must be free from carbonic acid, or the titration must be carried out in the boiling solution.

Organic acids of medium strength (oxalic acid, lactic acid, tartaric acid, etc.) cannot be titrated with indicators of the first class; those of the second class may be used, but it is preferable to employ those of the third class, the same conditions being observed for the normal alkalis as above.

Polybasic mineral acids of medium strength (phosphoric acid, sulphurous acid, etc.) cannot be titrated at all with indicators of the second class, but indicators of the first and third classes may be employed; different degrees of saturation occur in their titration, as will be seen below.

Weak acids, both organic and inorganic, can only be titrated, if at all, with indicators of the third class.

The *strong bases* (hydroxides of potassium, sodium, barium, calcium) can be titrated sharply with all indicators.

Bases of medium strength (ammonium hydroxide, amine bases) can be titrated sharply only with indicators of the first class and a few of the second, not with those of the third class.

Weak bases cannot be titrated sharply even with indicators of the first class, and not at all with those of the remaining classes.

J. Wagner[1] rejects the above classification of indicators in favour of a more scientific one, and divides them into the following groups:—A., Indicators with a univalent characteristic ion (1. anion: 2. cathion); B., those with a polyvalent ion (1. positive and negative ion = amphoteric electrolytes: 2. univalent and divalent anion or cathion). With A there are no intermediate colour changes, but these occur with B. Most indicators belong to the group A. 1., only a few to A. 2. and B. 2.

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[1] *Z. anorg. Chem.*, 1901, 27, 138.

Methyl orange belongs to group B. 1. This classification has not been generally adopted.

Many investigations on the sensitiveness of indicators have been carried out, but the results are frequently contradictory, and since the sensitiveness is so greatly affected by various other influences, such as temperature, dilution, presence of other substances (salts, alcohol, etc.), no broad and general conclusions can be deduced. The following remarks include the most reliable deductions.

Only in quite rare instances is it advisable to titrate with solutions of less than *N*/10 strength, because only very few indicators are sensitive enough to give a sharp colour change with 1-2 drops of the solution; iodo-eosin, in ethereal solution, is sufficiently sensitive to allow of the use of *N*/100 solutions.

Even with *N*/10 solutions there are differences with the ordinary indicators. In the absence of weak acids (carbon dioxide and sulphuretted hydrogen) the transition with phenolphthalein or well purified litmus is distinct, for most eyes, with a single drop; with methyl orange, two drops are necessary. This difference is illusory, however, since in practice it is seldom possible to completely exclude carbonic acid, and further, all indicators are less sensitive in hot solution.

With *N*/5 and stronger solutions, the sensitiveness of the three principal indicators is such that a single drop suffices to bring about the change of colour; other indicators are less sensitive.

Küster and Grüters[1] find that the orange (brownish) intermediate colour of methyl orange is always produced with the same hydrogen ion concentration, therefore the amount of acid required to effect this is roughly proportional to the volume of liquid. In 50 c.c. of water, 0·03 c.c. *N*/10 hydrochloric acid is required to bring about the change of colour; in 100 c.c., 0·06 c.c.; in 200 c.c., 0·12 c.c. Similarly, when chlorides are present (that is, more chlorine ions), more acid is required.

They state further, that the point of neutralisation can be determined most sharply by conductivity measurements, a method particularly applicable when precipitates or colorations make the use of coloured indicators impossible.

Solutions standardised with an indicator for hydroxyl ions, such as phenolphthalein, are not strictly correct when employed with an indicator for hydrogen ions, such as methyl orange (*cf.* p. 60).

Both alcohol and acetone lessen the sensitiveness of indicators, and the presence of considerable amounts of these substances in solutions to be titrated should, therefore, be avoided as far as possible; with phenolphthalein particularly, they cause great irregularity. If an addition of alcohol cannot be avoided, it is best to make a blank experiment to find how much acid or alkali is required to produce

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[1] *Z. anorg. Chem.*, 1903, **35**, 454.

the colour change in pure water containing the same amount of alcohol, and to allow for this in the titration. Alkaloids have sometimes to be titrated in strong alcoholic solution; in such cases lacmoid is the best indicator.

Neutral salts, which themselves do not alter the colour of the indicator, usually only affect the transition in titrating, when present in great concentration; such excess can as a rule be easily avoided. This is true more particularly of the alkali chlorides and sulphates, which are themselves formed in titrations. Lunge and Lohöfer[1] have shown that a certain amount of sodium chloride is necessary to get accurate results in titrating sodium silicate, sodium carbonate, and sodium sulphate with phenolphthalein, but that if present in large excess, it acts unfavourably, unless greatly diluted.

Warming often brings about a change of colour, even without the addition of acid or alkali. If, for instance, sodium hydroxide is added to sulphuric acid in the presence of methyl orange until a neutral orange tint is produced and the solution heated, the colour changes to a distinct yellow, and becomes orange again on cooling; therefore, in titrating acid with alkali in hot solution, using methyl orange as indicator, too little is required, and in titrating alkali with acid, too much. On the other hand, phenolphthalein in hot solution changes from red to colourless too soon. With methyl orange, the transition in hot solution is, as a rule, not sharp, and this indicator should, therefore, always be used at or only slightly above the ordinary temperature. Both phenolphthalein and litmus are less sensitive in hot solution than in cold, or rather the end-point is somewhat different, and due attention must be paid to this, since it is usually necessary to boil the solution to drive out the carbonic acid when using these indicators. For accurate estimations with litmus and with phenolphthalein, the solution should therefore always be boiled in the presence of a slight excess of acid, then allowed to cool, and the titration completed.

As already mentioned (p. 54), the action of hot solutions on glass must be taken into account and as far as possible avoided.

Theory of Indicators. The employment of indicators depends upon the fact that they change colour at a definite point on the addition of an acid or alkaline solution. This point may coincide with what is commonly known as "neutrality," but this is by no means always the case. If solutions of hydrochloric acid and sodium hydroxide are brought together, the change of colour will, it is true, take place with all indicators in practical use, when one molecule of sodium hydroxide is present for one of hydrochloric acid, so that the compound sodium chloride is formed. Since dilute solutions are always used, it is not to

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[1] *Z. angew. Chem.*, 1901, **14**, 1129; also, Küster, *Z. anorg. Chem.*, 1897, **13**, 145.

be assumed, according to modern views of solution, that only the compound NaCl actually exists in the solution, but rather that the greater part of it is dissociated into free $Na^{\cdot}$ and Cl' ions, just as the sodium hydroxide was previously, to a great extent, dissociated into $Na^{\cdot}$ and OH' ions, and the hydrochloric acid into $H^{\cdot}$ and Cl' ions. Neutralisation means rather that there is no appreciable amount of hydrogen ions which give the acid reaction, or of hydroxyl ions which give the alkaline reaction, in the solution, since the $H^{\cdot}$ ions of the hydrochloric acid have united directly with the OH' ions of the sodium hydroxide to form molecules of water.

In the presence of certain colouring matters even the smallest excess of an acid or of a base, that is, very small amounts of hydrogen or of hydroxyl ions, bring about a marked change of colour in one direction or the other, and the point of neutralisation is thus ascertained.

Ostwald[1] was the first to advance a theory of indicators; further contributions have been made by Küster,[2] Waddell,[3] Julius Wagner,[4] Bredig and Winkelblech,[5] Vaillant,[6] Roloff,[7] and Stieglitz.[8]

In regard to the theory of indicators, it will suffice to state that the indicators are or contain acids, or in some few cases bases, the undissociated molecules of which have a different colour from that of their ions.[9] Thus the undissociated molecules of the litmus acids are red, the anions blue, and since these acids are weak, in other words slightly dissociated, a mixture of the two colours results in aqueous solution. On addition of hydrogen ions, that is, acids, the litmus acids become practically undissociated, the blue anions disappear, and the red colour of the undissociated molecules appears. To effect this change, however, a certain minimum concentration of hydrogen ions is necessary, so that very weak acids such as carbon dioxide and sulphuretted hydrogen have practically no action; acetic acid, on the other hand, acts quite distinctly, unless its ionisation is so much decreased by the addition of sodium acetate that an insufficient amount of free hydrogen ions remains. When bases are added, salts of the litmus acids are formed which are largely dissociated, so that the blue colour of the ions is pronounced.

Phenolphthalein has a still weaker acid character; its undissociated molecules are colourless and its anions red. The few free hydrogen ions present in a solution are so greatly lessened in amount even by the weakest acids (carbon dioxide, etc.) that the red ions completely dis-

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[1] *The Scientific Foundations of Analytical Chemistry*, trans. by G. M‘Gowan, 2nd edition, 1900.

[2] *Z. anorg. Chem.*, 1897, **13**, 127.

[3] *J. Phys. Chem.* 1898, **2**, 171.

[4] *Z. anorg. Chem.*, 1901, **27**, 142.

[5] *Z. Electrochem.*, 1899-1900, **6**, 35.

[6] *Comptes rend.*, 1903, **136**, 1912.

[7] *Z. angew. Chem.*, 1902, **15**, 594 and 599.

[8] *J. Amer. Chem. Soc.*, 1903, **25**, 1112.

[9] The colour changes of indicators are regarded by some chemists as due to a rearrangement of the structure of the molecules, rather than to dissociation. *Cf.* A. G. Green and P. E. King, *J. Soc. Chem. Ind.*, 1908, **27**, 4.

appear and only the colourless molecules are left. Even the neutral aqueous solution shows no appreciable colour. The smallest trace of a strong base suffices to remove the hydrogen ions in combination with hydroxyl ions and to form a salt, the dissociation of which produces the red colour of the phenolphthalein anions. With weak bases, on the other hand, even with ammonium hydroxide, hydrolysis takes place, so that the free base and free colourless phenolphthalein molecules are formed ; in order to obtain a sufficient number of the red ions, more than the minimum quantity of the base must be added, so that the salt formation, and consequently the red coloration, is persistent.

Methyl orange is a fairly strong acid, the undissociated molecules of which are red and the anions yellow ; so many of the latter are present, even in a neutral solution, that a mixed colour results. On the addition of weak, in other words, slightly dissociated acids, the ionisation of methyl orange is not completely overcome, so that the mixed colour persists, the more so if a fairly large amount of the salt of the weak acid is formed in the titration ; the hydrogen ions are then not sufficient to cause the combination of the yellow anions of methyl orange to undissociated molecules. This recombination is brought about, on the contrary, on adding very small quantities of strong mineral acids, which are almost completely dissociated, and therefore yield sufficient hydrogen ions to render the methyl orange almost completely non-ionised, and so to produce the red colour.

More complicated cases are discussed under the individual indicators.

As a general rule, in titrating the same substances with the same standard solutions but with different indicators, the results obtained are not identical, because the changes of colour do not show identically the same " point of neutralisation " ; more hydrogen or hydroxyl ions may be necessary in one case than in the other to produce a change of colour. For example, a solution of hydrochloric acid which is exactly one-fifth normal when titrated with pure sodium hydroxide, using methyl orange as indicator, is not accurately one-fifth normal to phenolphthalein, even when the titration is carried out in the complete absence of carbonic acid, with continual boiling and all necessary precautions. For this reason normal solutions should as far as possible always be standardised with the same indicator as they are subsequently to be used with in practice. Even supposing it proved that, *e.g.*, the true point of neutralisation is obtained more correctly with phenolphthalein, all precautions being taken, than with methyl orange, nevertheless a standard acid to be employed subsequently for titrating in the cold with methyl orange must be standardised with the latter, and not with phenolphthalein ; accordingly, a substance such as sodium carbonate, which can be titrated with methyl orange, should be employed for standardising the acid, whereas potassium tetroxalate, which can only be titrated with phenolphthalein, ought not to be used if the standardised solution is to be employed with methyl orange.[1]

1. Methyl orange.

This indicator is the violet, crystalline *p*.dimethylaminoazobenzene *p*.sulphonic acid, $SO_3H.C_6H_4.N:N.C_6H_4.N(CH_3)_2$, or its yellow sodium salt, which is readily soluble in water. The latter is sometimes adulterated with dextrin; if this is the case, it does not form a clear solution, and should be rejected. The free acid cannot easily be adulterated, and is to be preferred. The sodium salt was manufactured for some time as a dye under the name of Poirrier's Orange No. 3, and also under the name of Helianthin; after it was recognised that it was useless as a textile dye, on account of its want of fastness, both names were transferred to other dyes, and for this reason ought no longer to be applied to the indicator. Lunge, who was the first to introduce it for this purpose,[2] suggested the name methyl orange, which is now generally adhered to, both for the free acid and for the sodium salt.

Next to litmus, methyl orange is no doubt the most widely used of all indicators, and in many cases it has completely displaced the former. It is true that it cannot be used in all instances, but in conjunction with phenolphthalein for certain purposes, it does in fact meet all the requirements of an indicator for alkalimetry and acidimetry.

Methyl orange is to be preferred to litmus also on the score of expense. According to Thomson's investigations,[3] 0·5 c.c. of a solution containing 0·15 g. per litre is required to give the same reaction as 0·5 c.c. of a litmus solution, which contains 20 g. of the dry extract in a litre, corresponding to about 60 g. of good litmus; the equivalent of 1 g. methyl orange is, therefore, 400 g. litmus. 1 kilo of methyl orange costs 16s., and 1 kilo of Ia litmus, at the price per 100 kilos, 3s.; inferior kinds of litmus are nominally cheaper, but, when the colouring power is taken into account, actually dearer. The 400 kilos of litmus which give the same result as the single kilo of methyl orange cost, therefore, £60, or seventy-five times as much as the equivalent amount of methyl orange. The various "purified" litmus preparations, azolitmin, etc., are much more expensive. Phenolphthalein costs 30s. and lacmoid 50s. per kilo.

For use, 1 g. of pure methyl orange is dissolved in 1 litre of water, and about two drops of this solution is added in each titration; this is sufficient to give a distinct yellow colour. If, owing to dilution during the titration, the colour becomes too faint, another drop of the indicator is added. Under no circumstances should too much of the indicator

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[1] *Cf.* Lunge, *Z. angew. Chem.*, 1904, **17**, 199.

[2] *Chem. Ind.*, 1881, **4**, 348; *Ber.*, 1878, **11**, 1994.

[3] *Chem. News*, 1883, **47**, 123.

be added at the beginning, since the transition is not sharp if the colour is too deep; for this reason many prefer to use a more dilute solution of methyl orange (about 1 to 10,000), so that the correct amount is not so readily exceeded. Methyl orange solutions sometimes become less sensitive when kept for a long time, and should then, of course, not be used.

It is imperative that the titrations should be made in the cold solution. In hot solutions the change of colour is only gradual, and the end-point cannot be recognised with any degree of certainty. If necessary, a temperature up to 30° is admissible, but it is better to work at the ordinary temperature.[1] According to Glaser,[2] the sensitiveness of methyl orange is not affected simply by titrating in hot solution, but only in the presence of neutral salts. Since, however, these are always formed in course of titration, the foregoing statement holds good. Large amounts of alcohol in the solution have also a disturbing effect. The sensitiveness is also lessened by dilution of the liquid.

The reddish-yellow colour of the indicator is changed to a pure yellow by alkaline liquids; this is effected not only by free alkali, but also by soluble carbonates, bicarbonates, sulphides, silicates, borates salts of arsenious acid, salts of fatty acids, and in general by the salts of all weak acids. The addition of a strong mineral acid (hydrochloric acid, sulphuric acid, nitric acid) to solutions of alkalis or of their salts with weak acids does not change the colour of the indicator, in spite of the fact that carbonic acid, sulphuretted hydrogen, or other weak acid is set free, until just before the formation of the normal salt of the strong acid, $NaCl$, Na_2SO_4, or $NaNO_3$, of course, with the exception of the colour which appears at the point where the acid comes into contact with the solution, and which disappears on stirring. Just before neutralisation, the very faint yellowish colour changes to a deeper brownish tint, which may be taken as the end-point of the reaction. On the addition of a further drop of the normal acid, the solution instantly becomes a decidedly red (carnation red) colour.

Küster (*loc. cit.*) has pointed out that even free carbonic acid in pure water, or solutions of neutral salts of strong acids, turns methyl orange red. Since, in the titration of carbonates as well as in most other cases where the work has not been carried out with the intentional exclusion of carbonic acid, the solution finally becomes saturated with carbonic acid, the titration should not be stopped at the brownish tint formerly regarded as the neutral colour, but acid should be added until the solution is definitely red. As a comparative guide for the colour change, a solution may be prepared by passing purified carbonic acid through pure water coloured with two drops of the indicator.

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[1] *Cf.* Lunge and Marmier, *Z. angew. Chem.*, 1897, **10**, 3.

[2] *Indikatoren*, loc. cit., p. 51.

If this plan is followed, it must not be overlooked that in titrating acid with alkali, the point of neutralisation will be different from that observed with the inverse procedure, and it is therefore always necessary to finish the titration in the same sense as that in which the strength of the solution was adjusted, titrating back eventually, if necessary.

Lunge is of opinion that the surest plan is to titrate, in both cases, until the brownish transition colour appears, and then to test whether the solution becomes decidedly red or yellow respectively on adding another drop, the last drop not to be included in the titration. The most trustworthy method would be to subsequently titrate back with the other volumetric solution until the transition colour again appears, and to subtract the amount required for this purpose, but this is not necessary in ordinary daily work.

According to Treadwell,[1] the most satisfactory plan is to titrate, in the cold, until the solution begins to change colour, drive out the carbonic acid by boiling, and then titrate the yellow solution, after cooling, until the brown tint reappears; but this is only necessary for $N/10$ acids, whilst with $N/5$, $N/2$, or $N/1$ acids, the alkali carbonates can be accurately titrated in the cold, by simply running in the acid until the yellow colour changes to reddish-orange (brownish). In technical analysis it is only necessary in quite exceptional cases to work with acids or alkalis weaker than $N/5$, so that the plan given by Treadwell is seldom called into consideration.

Lunge states that while carbon dioxide in distilled water does change the colour of methyl orange to reddish, although by no means to the same tint as that produced by a trace of hydrochloric acid or similar substances, yet in a solution of pure sodium chloride of the same strength as that usually formed in a titration, it gives rise to the brownish "transition colour," so that it is incorrect to titrate to a distinct red colour.

When normal or semi-normal acids are used, a single drop suffices, under all circumstances, to produce a change of colour which can be recognised with absolute certainty, even in artificial light; with $N/5$ acid, even an unskilled worker can, after a few experiments and comparisons with a standard colour, get results accurate to a single drop, but only in fairly good daylight or in white artificial light, preferably incandescent (Welsbach) light or acetylene light. A white surface should always be placed, not only under the flask in which the titration is being made, but also from 30 to 50 cm. round it; this applies to the use of all coloured indicators. In dull weather, or with ordinary gaslight, the results may easily be uncertain to one or two drops, and this uncertainty is correspondingly greater with $N/10$ acids; but there is seldom any object in

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[1] *Analytical Chemistry*, vol. ii., p. 427.

working with so weak an acid, even for scientific purposes, and in works' laboratories they are never used.

Although the change of colour from blue to red with litmus and still more, that from red to colourless, or conversely, with phenolphthalein, can be more readily recognised than that from yellow to brownish-red with methyl orange, these advantages are not appreciable with normal or semi-normal acids, or even with $N/5$ acid; as accurate results can be got with methyl orange as with the other indicators, after some practice. Since methyl orange has the very great advantage that the titrations are carried out at the ordinary temperature, any disturbing effect due to the glass being acted upon is eliminated; also, the estimation can be obviously carried out in less time than is required with other indicators with which boiling is necessary after each addition of acid.

With most other indicators the change of colour is sharper in cold than in hot solution, and it is therefore a disadvantage, as compared with the use of methyl orange, to have to carry out titrations with these in hot solution; also, because such titrations should, under no circumstances, be carried out in glass vessels.

The chlorides and sulphates of the heavy metals such as ferrous sulphate, ferrous chloride, copper sulphate, cupric chloride, and zinc sulphate, which are acid towards litmus, are neutral towards methyl orange.

From the above it is clear that methyl orange is much to be preferred to any other indicator for titrating *bases*, especially *total alkali*. On addition of mineral acids it indicates an extremely small amount of hydrogen ions, by the appearance of the red colour. It is equally applicable to the determination of alkali hydroxides, alkaline earths, ammonia, carbonates, and bicarbonates (for calcium carbonate and the like, it is, of course, necessary to add excess of acid and titrate back with alkali), to silicates, borates, salts of arsenious acid, and to sulphides, since sulphuretted hydrogen has no disturbing effect.[1] The fatty acids of soaps, etc., are without action, so that the amount of alkali in solutions of soap can be directly determined by titration.

Aniline, toluidine, and quinoline, which are indifferent towards litmus and phenolphthalein, behave as bases towards methyl orange, and can be fairly accurately titrated with this indicator;[2] more accurate results are obtained, in fact, as accurate as those with ammonia, with the aliphatic amine bases and with alkaloids in aqueous solution.

Aluminium, ferric, chromic, and zinc salts are neutral towards methyl orange, so that any content of free mineral acid can be determined, although only approximately.

Methyl orange is particularly suitable for the estimation of alkalinity

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[1] *Cf.* Lunge and Löhofer, *Z. angew. Chem.*, 1901, **14**, 1125.

[2] Lunge, *Dingl. polyt. J.*, 1884, **251**, 40; *Chem. Ind.*, 1893, **16**, 490.

in water analysis, *i.e.*, of the carbonates of alkalis, calcium, and magnesium.

As normal acid for the titration of alkaline solutions, hydrochloric acid, nitric acid, or sulphuric acid may be used, but not oxalic acid.

Methyl orange is, further, the best indicator for titrating the *strong mineral acids*, hydrochloric, nitric, and sulphuric; the titration is continued until the red colour gives place to the brownish mixed colour. As standard solutions, sodium or potassium hydroxide, which need not in this case be guarded from the absorption of carbon dioxide, or sodium carbonate may be used; the sensitiveness is not quite so great when the carbonate is employed. Baryta water may naturally also be used, although there is no object in doing so in this case. Since the transition from red to brownish is not quite so marked for many people as the inverse change, the addition, in doubtful cases, of a drop of normal acid to bring back the red colour may be used as a check.

Thiosulphuric acid behaves in the same way as the above strong mineral acids.

Methyl orange cannot be used for the titration of *organic acids*, whether strong (oxalic acid, tartaric acid, citric acid) or weak (acetic acid, etc.); in these cases the colour change is only gradual, and takes place before complete neutralisation.

Some mineral acids of medium strength behave peculiarly. With *sulphurous acid*, the change of colour with methyl orange takes place when the reaction $SO_2 + NaOH = NaHSO_3$ is just completed, and corresponds to the formation of the acid sulphite.[1] Therefore 1 c.c. of $N/1$ sodium hydroxide indicates, not one, but two equivalents (1 molecule) of $SO_2 = 0{\cdot}06406$ g. Inversely, normal sodium sulphite can be titrated with hydrochloric acid according to the equation $Na_2SO_3 + HCl = NaHSO_3 + NaCl$. The colour change takes place with phenolphthalein on completion of the reaction $SO_2 + 2NaOH = Na_2SO_3 + H_2O$, so that in this case 1 c.c. $N/1$ sodium hydroxide is equivalent to $0{\cdot}03203$ g. SO_2. Litmus gives intermediate values, and so cannot be used in this case.[2]

The *thiosulphates* are neutral to methyl orange, so that sodium thiosulphate does not react with it, while, on the contrary, normal sodium sulphite is alkaline, and the acid sulphite, neutral.

The *tribasic acids*, phosphoric acid and arsenic acid, give a neutral reaction with methyl orange when one of the hydrogen atoms is saturated, corresponding to the formation of the compound NaH_2PO_4,

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[1] Lunge, *Dingl. polyt. J.*, 1883, **250**, 530; *Z. angew. Chem.*, 1890, **3**, 563.

[2] *Cf.* Lunge, *loc. cit.*; Thomson, *Chem. News*, 1883, **47**, 123 and 184; Blaiez, *Comptes rend.*, 1886, **103**, 69.

etc.; they behave in this case as monobasic acids, whilst they are dibasic towards phenolphthalein, that is, the change of colour takes place on the formation of Na_2HPO_4, etc. Litmus gives indefinite results. Therefore, phosphoric acid and arsenious acid, like sulphurous acid, may be titrated with methyl orange as well as with phenolphthalein, but the alkali has double the saturation value with the former indicator that it has with the latter.

The behaviour of *nitrous acid* towards methyl orange is specially to be noted. The colouring matter is gradually destroyed by free nitrous acid, but small amounts, such as occur in chamber acid and in other commercial sulphuric acids, have scarcely any disturbing effect on the titration. In titrating nitrous vitriol or ordinary nitric acid containing oxides of nitrogen, on the other hand, the colour of the indicator disappears during the operation. This difficulty can, however, be very readily overcome in two ways. The indicator may either be renewed during the titration, or added only just before neutralisation, or else normal sodium hydroxide may be added in excess, then the indicator and the solution titrated back with normal acid. In other respects nitrous acid behaves towards methyl orange like the strong mineral acids; that is, sodium nitrite has a neutral reaction, and one molecule of nitrous acid is saturated by one molecule of sodium hydroxide.[1]

Alumina stands midway between acids and bases. Aluminium sulphate is neutral to methyl orange, but alumina itself (*in statu nascendi*) behaves as a base. In titrating sodium aluminate, either by itself or as a constituent of impure sodium carbonate, the change of colour of methyl orange only occurs when all the sodium carbonate and all the aluminate has been changed to normal sulphate. Suspended or colloidal dissolved aluminium hydroxide reacts only slowly and incompletely, in the cold, and the titration should be carried out at about 40°, the change of colour taking place when the alumina has been converted into $Al_2(SO_4)_3$.[2] The Na_2O can thus be determined in sodium aluminate by first titrating with normal acid in the presence of phenolphthalein (which is indifferent to alumina), and then the alumina with methyl orange.

Methyl orange can sometimes be used in conjunction with a second indicator, *e.g.* phenolphthalein, to estimate different constituents in one and the same solution, as in the analysis of sodium aluminate. Thus, the amount of sodium carbonate in caustic soda can be determined with sufficient accuracy for technical purposes, by titrating first with phenolphthalein till colourless and then with methyl orange

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[1] Lunge, *Z. angew. Chem.*, 1903, **16**, 59.

[2] *Cf.* Cross and Bevan, *J. Soc. Chem. Ind.*, 1891, **10**, 202; also, Lunge, *J. Soc. Chem. Ind.*, 1891, **10**, 314.

till the red colour appears; the first indicator gives all the sodium hydroxide and half the sodium carbonate, corresponding to the formation of $NaHCO_3$, the second gives the other half of the carbonate.[1] In the analysis of soap solutions Filsinger and Elsner first determine the sodium combined with fatty acids, with normal acid and methyl orange and then the sodium chloride with silver nitrate, in the same solution, using potassium chromate as indicator.

A mixture of methyl orange and phenolphthalein is coloured red both by acids and bases, but retains its clear yellow colour in neutral solutions.[2]

The mother substance of methyl orange, dimethylaminoazobenzene, which is soluble in alcohol, has been recommended by B. Fischer and Philipp[3] instead of methyl orange; according to both Lunge[4] and Thomson,[5] it offers no advantage over the latter, and is less sensitive;[6] this is also true of the ethyl compound (ethyl orange), which has been preferred by some to methyl orange.

2. Litmus.

Litmus is supplied in small bluish cubes, which contain the actual colouring matter, the blue potassium salt of the red azolitmic acid, mixed with varying amounts of calcium carbonate, gypsum, etc., and sometimes adulterated with indigo. Litmus usually contains 4 to 5 per cent. of the actual colouring matter.

The general method formerly used in making litmus solution consisted simply in pouring distilled water over the cubes (preferably without grinding them), pouring off the first extract, which contained excess of potassium carbonate, and using the subsequent extracts. As this solution required a fairly large amount of acid to change the blue colour to the neutral violet tint, it was customary to divide it into two equal parts, and to add hydrochloric or other strong acid carefully to one half until it became distinctly red (brick-red) and then mix it with the other half; the mixture was of a violet to wine-red colour and sensitive both to acids and alkalis.

Attempts have been made to overcome the defects of the solution prepared as above, especially its lack of sensitiveness, by various improvements; they all add, however, to the cost of an initially expensive indicator, and have accordingly not been adopted in technical laboratories. According to Mohr-Classen,[7] the litmus cubes should first be boiled three or four times with 85 per cent. alcohol, to remove a foreign colouring matter. The first aqueous extract is also to be

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[1] *Cf.* Lunge, *Z. angew. Chem.*, 1897, **10**, 41.

[2] Gawalowski, *Zeit. anal. Chem.*, 1883, **22**, 397.

[3] *Arch. Pharm.*, 1885, **23**, 434.

[4] *Ber.*, 1885, **18**, 3290.

[5] *J. Soc. Chem. Ind.*, 1887, **6**, 196.

[6] Lunge and Marmier, *Z. angew. Chem.*, 1897, **10**, 3.

[7] *Lehrbuch der chemischen analytischen Titrirmethode*, 7th edition, 1896, p. 75.

rejected and hydrochloric acid added, drop by drop, to the subsequent extracts until they assume a violet colour. The most sensitive solution is prepared by first adding an excess of dilute sulphuric acid, boiling to expel carbon dioxide, and then adding baryta water, drop by drop, until a violet colour is produced.

Lüttke[1] recommends treating the aqueous extracts with hydrochloric acid and then removing the latter by dialysis. According to Stolba, the colouring matter should be transferred to linen and washed, then extracted with alkaline water and the solution neutralised with acid. Reinitzer[2] states that only certain kinds of commercial litmus can be used for analytical purposes. These should be extracted with water and concentrated hydrochloric acid added, drop by drop, to the boiling solution until, after seven to eight minutes' boiling, a distinct red colour is obtained. The solution is then allowed to cool and an equal volume of strong alcohol added.

A specially pure litmus colouring matter, soluble in water, has been introduced under the name of *Azolitmin;* it is scarcely more sensitive than good litmus solution, and is too expensive for use in works. According to Böckmann, no plan in which too much colouring matter is lost can under any circumstances be used technically, since a single works may often use 100-150 kilos of litmus.[3]

Litmus solution spoils when kept in closed vessels, doubtless owing to the development of anaërobic microbes. It can, however, be kept good as long as desired by allowing free access of air, which may be done by keeping it in bottles which are not quite filled, the entrance of dust being prevented by a loose cap or by a pellet of cotton wool. The most convenient plan is to provide the bottle with a loosely fitting cork, in which a small pipette, for taking out any desired quantity of solution, is inserted (Fig. 37). The same method of storage, but using a well-fitting cork, is also strongly to be recommended for other indicators.

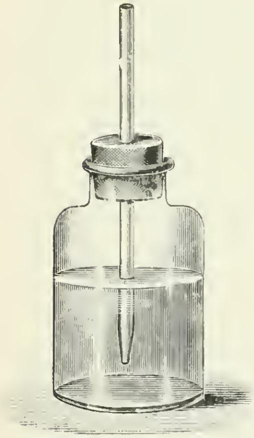
FIG. 37.

Since there is no objection to keeping litmus solution with access of air, addition of phenol and similar substances is unnecessary.

Properly prepared litmus solution, provided it is neutral, is an excellent indicator for bases, which change the violet colour to blue, as well as for strong acids, which give a pure red (yellow-red) colour. If the solutions in question are absolutely free from carbon

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[1] Cf. *Lehrbuch der chemischen analytischen Titrirmethode*, 7th edition, 1896, p. 97.

[2] *Z. angew. Chem.*, 1894, **7**, 547.

[3] For a special method of preparing litmus solution, *cf.* Förster, *Z. anal. Chem.*, 1889, **28**, 428.

dioxide, free alkalis can be titrated with acids and free, strong acids with bases (potassium, sodium or ammonium hydroxide), with the greatest accuracy. Reinitzer has shown that the greatest sensitiveness is obtained with litmus, as is the case with methyl orange, by titrating in the cold—a condition, however, which is not readily compatible with the complete absence of carbon dioxide, which is necessary with this indicator. Lunge[1] has shown that the statement of Reinitzer, that litmus is eight times as sensitive as methyl orange, is greatly exaggerated; under the most favourable circumstances the sensitiveness is only double that of methyl orange, and the advantage of this greater sensitiveness only arises in exceptional circumstances, under the ordinary conditions of work.

Besides the three mineral acids, sulphuric, hydrochloric and nitric, oxalic acid also gives an equally sharp end-reaction with litmus. It is in all cases advisable to titrate until a distinct blue colour is produced and not to stop at a violet coloration, because the transition from red to violet is not sharp, whilst that from violet to blue can be determined to a single drop.

Litmus behaves quite differently towards weak acids. *Carbonic acid* causes a pale port-wine red tint which renders the transition from the blue, produced by alkalis, to the clear red produced by acids, indistinct. The direct titration of alkaline carbonates cannot therefore be carried out in the cold, but the solution must be heated to boiling as soon as it turns red; if it becomes blue again, as is generally the case, more acid must be added and the liquid again boiled, and this must be continued until the colour is permanent and distinctly red. This makes the operation very tedious. The whole titration should be carried out in the boiling solution, were this possible, but for obvious reasons the burette cannot well be fixed above the boiling liquid itself. Since every kind of glass, even the so-called "resistance glass" and hard Bohemian glass, give up alkali to boiling alkaline liquids, porcelain vessels should be employed for the titration; but in using them, it should not be overlooked that on continued boiling in basins, small losses by spurting may readily occur without being noticed.

Reinitzer has shown that litmus is much less sensitive in hot than in cold solutions; also, that even lime water and baryta water, as well as the aqueous litmus extract itself, contain sufficient carbonic acid to cause inaccurate results on titrating in the cold.

For the above reasons, recourse must be had to an indirect method for titrating carbonates, if accurate results are desired. This is attained by adding an excess of standard acid, boiling the solution to drive out all the carbon dioxide, and then titrating back with standard alkali; the standard alkali must be free from carbon dioxide, and the absorption

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[1] *Z. angew. Chem.*, 1894, 7, 733.

of carbon dioxide during cooling and titrating must be avoided. Reinitzer has suggested that the cooling should be accelerated by means of a jet of water, but this is scarcely practicable with porcelain basins and is likely to cause breaking with most kinds of glass. In the majority of cases it is preferable to titrate the solution whilst hot, even at the expense of some loss in sensitiveness.

Since the omission of any of the above precautions does away with the greater sensitiveness of the reaction with litmus, and since the necessity of boiling the solution leads to great loss of time, it is not surprising that litmus, which was formerly in general use for the titration of carbonates, has been to a very large extent discarded in favour of methyl orange. Phenolphthalein is open to exactly the same objections as litmus and has accordingly in no way replaced it.

Sulphuretted hydrogen destroys the colouring matter of litmus; in estimating sulphides, therefore, it is necessary to add excess of acid, boil and titrate back with alkali.

Boric acid, *phosphoric acid*, etc., do not give a sharp end-reaction, and the same is true of *sulphurous acid* (*cf.* methyl orange, p. 65), so that the salts of these acids cannot be titrated with litmus; on the other hand, *silicates* give a good end-reaction, as the precipitated silicic acid has no action on litmus.

Weak bases, such as aniline, quinoline, and many alkaloids, have no action whatever on litmus.

It is much more difficult to recognise the change of colour with accuracy in artificial light than in daylight. The suggestion to titrate in monochromatic light (sodium flame) cannot be regarded as practicable.

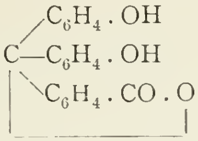
To summarise, litmus can be used very satisfactorily for the titration of free, strong acids, but if great accuracy is required, the titration must be made in the cold and with alkalis (sodium and potassium hydroxides, ammonia, baryta water) free from carbon dioxide. The material of the vessel in which the titration is done is then not of much importance. But even in this case litmus is only preferable to methyl orange when *N*/10 alkalis are used, which is very seldom the case in practice and if the precautions with regard to the exclusion of carbon dioxide are carefully observed throughout the whole operation. This is, however, very difficult, as even baryta water may contain sufficient carbon dioxide in solution to make the end-reaction quite inaccurate.

Litmus cannot be used for the titration of salts of sulphurous, boric, and phosphoric acids.

Litmus may be used for the titration of carbonates, but is by no means to be specially recommended. It can only be used if the carbon dioxide is driven out by continued boiling, and even then an accurate result is only obtainable if the instructions given above are followed.

3. Phenolphthalein.

Phenolphthalein is a triphenylmethane derivative, being the anhydride of dihydroxy-triphenyl carbinol-carboxylic acid, and has the structural formula—



It was introduced as an indicator by Luck.[1] It is a white crystalline powder, melting at 150°, sparingly soluble in water but readily in alcohol. It is used in 1 per cent. solution of 90-95 per cent. alcohol, about two drops being added for each titration; an excess is not harmful, as is the case with methyl orange. The colourless solution of phenolphthalein is reddened by hydroxyl ions, that is, even by the smallest trace of an alkali hydroxide, and on this account it is one of the most sensitive of indicators; its use is, however, very greatly restricted, owing to its being too sensitive to the weakest acids, more particularly carbon dioxide, which decolorise the red alkaline solution, just as strong acids do.

The transition from red to colourless, produced by acids, is not so delicate as the inverse change, which is very distinct even in artificial light.

Phenolphthalein cannot be employed for the titration of ammonia, nor in the presence of ammonium salts; also, it cannot be used if any considerable amount of alcohol is present (*cf.* p. 57).

The real utility of phenolphthalein is, exclusive of its use as a qualitative test for alkalis and alkaline earths, in the titration of the *weaker acids*, from chromic acid and oxalic acid down to acetic acid. Methyl orange is quite useless in these cases, and litmus is less sensitive. It is preferable to use barium hydroxide solution for the titration, adopting all necessary precautions; if potassium or sodium hydroxide is used, they must be quite free from carbon dioxide, otherwise the estimation is altogether inaccurate. It is not always possible to titrate in hot solution so as to exclude carbon dioxide, *e.g.*, with acetic acid, on account of its volatility, nor with citric acid, etc., according to Thomson, since when heated, in solution, a normal salt alkaline to phenolphthalein is formed, so that inaccurate results are obtained. The fixed organic acids can be titrated with sodium hydroxide containing a little carbonic acid, if the estimation is made in the boiling solution; this is best done by adding a slight excess of the alkali, boiling until the solution has become permanently red, and then titrating back with standard acid.

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[1] *Z. anal. Chem.*, 1877, **16**, 3202.

This operation is always tedious, and there is no object in adopting it for the titration of strong mineral acids or alkalis, which are so much more conveniently titrated with methyl orange in cold solution.

The point of neutralisation is reached with phosphates and arsenates when the compounds Na_2HPO_4 and Na_2HAsO_4 are formed; with sulphites the normal salt is neutral towards phenolphthalein.

The red phenolphthalein solution is decolorised by a number of substances which are very weakly or scarcely perceptibly acid towards litmus, such as boric acid, arsenious acid, potassium bichromate, and even gum arabic.

Boric acid can only be accurately titrated with phenolphthalein in the presence of glycerine;[1] chromic acid can be very accurately estimated with this indicator, the change of colour taking place on the formation of K_2CrO_4.

For the estimation of the *hydroxides of the alkalis and alkaline earths*, phenolphthalein is undoubtedly the best and most sensitive indicator, if these are present alone in solution and free from carbonate; as far as the alkalis are concerned, however, this is seldom the case in practice. In the presence of alkaline carbonates, the formation of bicarbonates must be taken into acount (cf. *infra*); with the alkaline earths, the carbonates of which are practically insoluble in water, it is possible, according to C. Winkler (confirmed by Küster and Lunge, cf. *infra*), by the careful addition of hydrochloric acid, to strike the point when all the calcium or barium hydroxide is just saturated. The small amount of carbon dioxide which is set free from the carbonates by the next drop or two of standard acid, decolorises the phenolphthalein and shows the end of the reaction. This method can also be adapted for the estimation of alkali carbonates in the presence of alkali hydroxides by adding chloride of barium in excess to the solution, all the carbonic acid being thus combined with the barium; this is, in fact, the most accurate method for the purpose, but the hydrochloric acid must be added slowly to the mixture, drop by drop, with continual thorough stirring or shaking.

For the titration of *alkaline carbonates*, a distinction must be made between titrating in hot and cold solution. In hot solution, carbon dioxide is removed, and accordingly phenolphthalein acts exactly like litmus, but the solution requires longer boiling. The change of colour is much more striking than with methyl orange and the sensitiveness is also theoretically greater, but the necessity of long boiling makes the advantage, with regard to sensitiveness, quite illusory when glass vessels are used, owing to the unavoidable action of the hot solution on the latter; also the titration takes much longer than with methyl orange. There is, therefore, no object in using phenolphthalein in this case.

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[1] *Z. angew. Chem.*, 1896, **9**, 561; 1897, **10**, 5; 1902, **15**, 733.

In the cold, so long as the carbon dioxide formed by the reaction $Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$, has more than sufficient sodium carbonate at its disposal to form bicarbonate, the red colour persists; when, however, it is all changed to $NaHCO_3$ and free carbonic acid is formed, the colour disappears, since it is destroyed by free carbon dioxide. It was formerly supposed that this method could be used directly for determining the amount of alkali in normal carbonates,[1] each equivalent of normal acid of course indicating two equivalents of alkali ($Na_2CO_3 + HCl = NaCl + NaHCO_3$), and the reaction is still made use of, especially for estimating sodium carbonate in presence of sodium hydroxide, by first titrating with phenolphthalein till the solution becomes decolorised, when all the hydroxide and half the carbonate are saturated, and then either completing the titration in boiling solution, or, more conveniently (*cf.* p. 66), by adding methyl orange and finishing the titration cold. The result of the second titration, multiplied by two, gives the amount of Na_2CO_3 originally present; the amount of NaOH is obtained from the difference between the first and second titrations.

It has been shown by Küster[2] that this estimation is not quite accurate, and he has given an explanation of his results, based on the electrolytic dissociation theory. Lunge[3] has shown that the method is sufficiently accurate for the estimation of a small quantity of sodium carbonate in the presence of much sodium hydroxide, *e.g.*, in caustic soda (*cf.* p. 66), but not for much carbonate, with a small quantity of hydroxide. This point was subsequently more accurately investigated by Lunge and Lohöfer.[4] It was found that, as previously shown by Küster, the titration gives results nearer the correct value if sodium chloride is added, the introduction of ions of the same kind hindering the ionisation of the sodium carbonate; if the solutions are not too concentrated, results accurate to 0·1 c.c. are obtained if the ratio of sodium chloride to sodium carbonate is at least 1·75 to 0·5 molecules. This holds with increasing amounts of sodium chloride, but when ten molecules and upwards are present for 0·5 molecule of carbonate, it is found that too little hydrochloric acid is used, which is in accord with the ionisation theory. This explains why, in the titration of caustic soda—that is, a large quantity of hydroxide and a little carbonate—the latter can be accurately estimated by Warder's method, since in this case a sufficient amount of sodium chloride is formed from the hydroxide, before the action of the hydrochloric acid on the carbonate begins.

Lunge has recently found that, in order to get accurate results, it is not only necessary to observe the above condition (excess of sodium chloride), but that the titration must be carried out in as concentrated a

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[1] Warder, *Amer. Chem. J.*, 1881, **3**, 55.

[2] *Z. anorg. Chem.*, 1897, **13**, 141.

[3] *Z. angew. Chem.*, 1897, **10**, 41.

[4] *Ibid.*, 1901, **14**, 1125.

solution and at as low a temperature (little over 0°) as possible; all of these conditions diminish the ionisation of the sodium carbonate. Further, the titration must be done rapidly, so as to avoid escape or absorption of carbon dioxide.

The estimation of sodium carbonate in the presence of sodium bicarbonate, using phenolphthalein as indicator, is carried out in the same way. The titration is done in the cold until the solution becomes decolorised, which takes place when half the carbonate present is changed into bicarbonate; the liquid is then heated to boiling, and titrated till the colour again disappears. The number of c.c. of acid required for the first decolorisation, multiplied by 2, gives the amount of carbonate present, and the difference between this and the total c.c. required gives the number of c.c. corresponding to the bicarbonate.[1] A simpler plan is to carry out the first titration in the cold solution with phenolphthalein, and the second likewise in the cold, after the addition of methyl orange.

Thomson, and subsequently Lunge and Lohöfer, have shown that *sodium silicate* cannot be titrated alone, with phenolphthalein as indicator, with any degree of accuracy; the change of colour is gradual and cannot be sharply determined, and it always takes place long before the completion of the reaction $Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$. Sharp results are obtained, however, in accord with this equation if much sodium hydroxide is present, from which sodium chloride can be formed, or if sodium chloride is added directly, apparently because sodium silicate is hydrolytically dissociated and acts towards phenolphthalein as a weak acid as long as it is present as hydrosol; but in presence of sodium chloride, the silicic acid passes into the hydrogel, and has then no action on phenolphthalein.

Titration with phenolphthalein in alcoholic solution has been studied by Hirsch[2] and by Schmatolla.[3]

Potassium or *sodium sulphide* can be titrated with acid in the presence of phenolphthalein. The colour disappears when half the sodium has been changed to NaHS, so that the relations are completely analogous to those with carbonates:—

$$HCl + Na_2S = NaHS + NaCl.$$

Aniline, *toluidine*, *quinoline*, and most alkaloids have no action on phenolphthalein, and their salts can therefore be titrated with normal sodium hydroxide like free acids.

Thomson[4] has collected many of the above facts in the following table (altered in some particulars by Lunge). The figures give the number of hydrogen atoms, in the acid molecule, replaced by sodium

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[1] *Cf.* Kippenberger, *Z. angew. Chem.*, 1894, **7**, 495.

[2] *Ber.*, 1902, **35**, 2374.

[3] *Ibid.*, 1902, **35**, 3905.

[4] *J. Soc. Chem. Ind.*, 1887, **6**, 198.

when the solution becomes neutral; cases in which the end-point cannot be sharply recognised with the indicator are represented by a line in the table.

Table of the Basicity of Acids towards different Indicators in titrating with Sodium Hydroxide.

Acids.	Methyl orange.	Phenolphthalein.		Litmus.	
	In the Cold.	In the Cold.	Boiling.	In the Cold.	Boiling.
Sulphuric Acid, H_2SO_4	2	2	2	2	2
Hydrochloric Acid, HCl	1	1	1	1	1
Nitric Acid, HNO_3	1	1	1	1	1
Thiosulphuric Acid, $H_2S_2O_3$	2	2	2	2	2
Carbonic Acid, H_2CO_3	0	1 (*cf.* p. 72)	0	—	0
Sulphurous Acid, H_2SO_3	1	2	—	—	—
Phosphoric Acid, H_3PO_4	1	2	—	—	—
Arsenic Acid, H_3AsO_4	1	2	—	—	—
Arsenious Acid, H_3AsO_3	0	—	—	0	0
Nitrous Acid, HNO_2	1 (*cf.* p. 66)	1	—	1	—
Silicic Acid, H_2SiO_3	0	—	—	0	0
Boric Acid, H_3BO_3	0	—	—	—	—
Chromic Acid, H_2CrO_4	1	2	2	—	—
Oxalic Acid, $H_2C_2O_4$	—	2	2	2	2
Acetic Acid, $HC_2H_3O_2$	—	1	—	1 (about)	—
Butyric Acid, $HC_4H_7O_2$	—	1	—	1 ,,	—
Succinic Acid, $H_2C_4H_4O_4$	—	2	—	2 ,,	—
Lactic Acid, $HC_3H_5O_3$	—	1	—	1	—
Tartaric Acid, $H_2C_4H_4O_6$	—	2	—	2	—
Citric Acid, $H_3C_6H_5O_7$	—	3	—	—	—

The table holds for ammonium hydroxide as well as for sodium hydroxide, with the exception of phenolphthalein, which, as stated, does not give a sharp end-point with the former.

Other Indicators.

Very many other indicators are known, but they are, as a matter of fact, superfluous for most purposes; their supposed advantages are in part quite illusory and in part counterbalanced by drawbacks. The following are the most important.

Indicators of the first class:—

Lacmoid, prepared and recommended as an indicator by Traub and Hock[1] and by Förster,[2] is used in alcoholic solution. It has far more analogy with methyl orange than with litmus, resembling the latter only in being turned red by acids and blue by alkalis. It is considerably more sensitive than litmus, especially when used as test paper. It is not suitable for the titration of carbonates, sulphites, and sulphides, but can be used for borates and silicates. Neutral chromates react strongly alkaline to it, acid chromates neutral, so that it can be used, in the form

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[1] *Ber.*, 1894, **27**, 2615.

[2] *Z. angew. Chem.*, 1890, **3**, 163.

of test paper, to detect the presence of neutral chromate mixed with acid chromate (litmus paper cannot be used for this purpose.) It is useless for titrating organic acids, and cannot be used in presence of nitrous acid or of sulphuretted hydrogen.

According to Messner,[1] lacmoid is the best indicator for titrating cinchona alkaloids in alcoholic solution.

Blue lacmoid paper is also distinctly blue in artificial light, whilst litmus paper is violet ; the former is scarcely more sensitive than the latter. Red lacmoid paper, which must be protected against access of air, is more sensitive than red litmus, and retains its colour better.

Various *azo-dyes* behave like methyl orange, but are all inferior to it. Reference has already been made to dimethylaminoazobenzene, and *ethyl orange* (p. 67). *Tropäolin* OO (orange IV., diphenylamine orange) was recommended by von Miller[2] even before the introduction of methyl orange. Like methyl orange, it is turned red by the stronger acids and is not altered by carbonic acid ; it is, however, so much less sensitive than methyl orange that is must be regarded as quite useless for work of any degree of accuracy. *Diaminoazotoluenesulphonic acid,* described by Troeger and Hille,[3] seems to act very similarly to methyl orange.

Rubrescin is a new indicator discovered by Rosenfeld and Silber.[4] It is prepared by melting together 50 g. resorcinol and 25 g. chloral hydrate in an oil bath at 160°, the powdered mass being purified by treatment with warm chloroform. The indicator has a strongly acid character, and is much more sensitive towards alkalis than phenolphthalein ; one drop of *N*/10 sodium hydroxide in 100 c.c. of water retains its red colour with this indicator for an hour, whilst the red colour of phenolphthalein disappears in a few seconds under the same conditions. With borax and sodium carbonate it is equally sensitive. If the colour is not very intense it disappears on addition of acid, if of greater intensity it changes to yellow.

Iodo-eosin, also known commercially as erythrosin or pyrosin, is tetraiodofluorescein. It is not used in ordinary alkalimetry, but for the detection of very small amounts of alkali, as, for example, that dissolved from glass by the action of water.[5] A solution of 2 mg. in 1000 c.c. of carefully purified ether containing a little water, is used ; 10-20 c.c. of the solution is added to 50-100 c.c. of the solution to be tested and the mixture shaken. In the presence of free alkali the lower layer becomes red ; the colour disappears on addition of acid. This indicator may also be used colorimetrically, and is particularly suitable for the estimation of alkaloids. According to Glücksmann,[6] it is indifferent towards carbonic acid.

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[1] *Z. angew. Chem.*, 1903, **16**, 449.

[2] *Ber.*, 1878, **11**, 460.

[3] *J. prakt. Chem.*, 1903 [2], **68**, 297.

[4] *Chem. Zeit. Rep.*, 1902, **26**, 130.

[5] Mylius and Förster, *Z. anal. Chem.*, 1892, **31**, 248.

[6] *Chem. Centr.*, 1902, **II**, 476.

Ferric salicylate is recommended by J. Wolf as an indicator for strong acids, in the presence of boric acid, and thus permits of the subsequent determination of the latter. On saturation with sulphuric acid, the violet colour changes to an alizarin orange. According to Lunge,[1] this indicator is in no way superior to methyl orange.

Congo red is turned blue by acids; the red colour is restored by alkalis. Free carbonic acid colours it bluish-violet, acid salts have no action, so that it might be employed, *e.g.*, for estimating free acid in aluminium sulphate. Although this indicator was at first regarded as of considerable value, it was soon found to be useless for most purposes and not very sensitive. According to Thomson,[2] it is unreliable, both because the change of colour is not sharp and because the uncertainty of the end-point is increased by the presence of salts, such as sulphates, chlorides, and nitrates of the alkalis; also, it is less sensitive for the detection of free acid than all the other indicators that are suitable for this purpose. The former opinion, that Congo red test paper is as good as or even preferable to litmus paper, has been similarly disproved. Congo red cannot be used in hot solution, nor in the presence of nitrous acid, nor for the titration of weak acids.

Para-nitrophenol has been recommended by many workers, especially by Spiegel,[3] in place of methyl orange. It has a yellow colour in alkaline solution, which disappears on neutralisation with strong acids. It is only slightly acted upon by carbonic acid, but distinctly more so than methyl orange;[4] Glaser (p. 55) therefore includes it among indicators of the second class. For this reason it is by no means so useful as methyl orange; further, the disappearance of the yellow colour or its first appearance takes place so gradually that it can only be observed with accuracy by a quick eye in clear daylight, and then only with considerable effort. According to Glaser, it can be used advantageously for indicating the continued alkaline reaction after the addition of soda, etc., to the water in a steam boiler, because, unlike other indicators, it is not decomposed even at 150°.

Goldberg and Naumann[5] obtained better results by using a fairly large amount of the indicator; they confirm its sensitiveness to carbonic acid, however, as well as the observation that the change of colour is much more difficult to recognise than with methyl orange.

Ortho-nitrophenol is, according to Lunge,[6] less useful than the para-compound.

Tincture of *Cochineal*, when properly prepared, is, according to

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[1] *Z. angew. Chem.*, 1904, **17**, 203.

[2] *J. Soc. Chem. Ind.*, 1887, **6**, 175.

[3] *Ber.*, 1900, **33**, 2640; *Z. angew. Chem.*, 1904, **17**, 715.

[4] Lunge, *Z. angew. Chem.*, 1903, **16**, 560; 1904, **17**, 202.

[5] *Z. angew. Chem.*, 1903, **16**, 644.

[6] *Ibid.*, 1904, **17**, 202.

Dupré,[1] almost as sensitive as phenolphthalein; it is but little affected by carbon dioxide.

Indicators of the third class:—

Turmeric is only of importance as a test paper. The yellow paper is turned red-brown by alkalis, but it is much less sensitive than litmus. It is of practical value for the titration of dark-coloured solutions of organic acids for which other indicators cannot be used, and in the detection of boric acid.

Poirrier's blue, C 4B, would fill a great blank, if it could be more generally employed.[2] Its colour is altered even by the very weakest acids, which have no effect on any of the other indicators. Borax, which is alkaline to all other indicators, has an acid reaction to Poirrier's blue, which only disappears on complete neutralisation of the boric acid. In the same way, monohydrogen salts of phosphoric acid, which are alkaline to litmus and methyl orange and neutral to phenolphthalein, give an acid reaction, and in this case also the change of colour only takes place on complete neutralisation of the phosphoric acid. Arsenic acid behaves in an exactly analogous way. It has been proposed to use this indicator for the determination of alkali hydroxide in the presence of alkali carbonate, but since this is only practicable in concentrated solution, with any degree of accuracy, on account of the great irregularity due to the hydrolysis of the indicator, it is no real value for this purpose.

It is evident from the above that different indicators not infrequently give different reactions with one and the same substance. Thus, neutral potassium chromate and sodium acetate are neutral to phenolphthalein, weakly alkaline to litmus and turmeric, whilst the latter is acid to Poirrier's blue. Monohydrogen salts of phosphoric and arsenic acid, which are alkaline to litmus and methyl orange, are neutral to phenolphthalein, and acid to Poirrier's blue. Borax is acid to Poirrier's blue, but alkaline to all other indicators. Boric acid, which turns turmeric paper red, similarly to alkalis, has no action on methyl orange, so that the acid can be titrated with borax solution, using methyl orange as indicator. Urine, which is usually acid to litmus and phenolphthalein, is strongly alkaline to lacmoid. Fresh milk, which gives a neutral or amphoteric reaction with litmus, is distinctly alkaline to lacmoid and distinctly acid to phenolphthalein.

The sensitiveness of the more important indicators has been determined by precise physical methods both by Friendenthal[3] and by Salm.[4]

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[1] Private communication to Prof. Lunge.

[2] Engel and Ville, *Comptes rend.*, 1885, **100**, 1073; Engel, *Z. anal. Chem.*, 1888, **27**, 30.

[3] *Z. Electrochem.*, 1904, **10**, 113.

[4] *Ibid.*, 1904, **10**, 341; *Z. physik. Chem.*, 1906, **57**, 471.

Test Papers.

These are ordinarily employed for indicating the acidic or basic character of a liquid, and for this purpose are made, conversely, either weakly basic or acidic. Fine white writing paper is usually prescribed for their preparation (Mohr), because a drop of liquid placed on it does not spread too much. According to Glaser, filter paper is preferable for use with solutions which are coloured or which contain salts, which disturb the reaction, since in such cases the drop spreads out, leaving the colouring matter or salt in the centre, and a sharper reaction is obtained at the edge. Paper used for this purpose must previously be well washed and dried.

When writing paper is used, the solution of the indicator is spread on it, whilst filter paper is saturated by dipping it into the solution; the paper is dried by hanging it up in an atmosphere free from acid and ammoniacal vapours. Papers prepared with indicators of the first class are most suitable for weak bases, with those of the third class for weak acids; for strong bases and acids they are all equally sensitive.

Glaser gives the following table, showing at what dilution the acid or alkaline reaction just ceases to be noticeable:—

	Sulphuric Acid.	Sodium Hydroxide.	Ammonium Hydroxide.
Yellow Methyl orange paper .	$\frac{1}{1000}N$.	...	...
Congo Red paper . . .	$\frac{1}{10000}N$.	...	...
Blue Lacmoid paper . .	$\frac{1}{10000}N$.	...	...
Red Lacmoid paper . .	...	$\frac{1}{2000}N$.	$\frac{1}{2000}N$.
Blue Litmus paper . . .	$\frac{1}{10000}N$.	...	...
Red Litmus paper . . .	...	$\frac{1}{5000}N$.	$\frac{1}{3000}N$.
Violet Azolitmin paper . .	$\frac{1}{4000}N$.	$\frac{1}{6000}N$.	$\frac{1}{5000}N$.
Turmeric paper . . .	...	$\frac{1}{3000}N$.	$\frac{1}{3000}N$.
Phenolphthalein paper . .	...	$\frac{1}{2000}N$.	$\frac{1}{2000}N$.

He states, however, that the sensitiveness may, in individual cases, be very different from the figures given above, owing to the method of preparation of the test papers.

Test papers are mostly used for the qualitative detection of acids or bases; for quantitative purposes they are used only with coloured liquids, or with such as destroy indicators.

Test papers should always be kept in well-closed vessels, and protected from light, either in tightly fitting wood or metal boxes, or in glass bottles covered with black paper; they are soon spoiled by moisture.

Litmus paper, blue, red, and violet (neutral), is by far the most widely used test paper. To prepare it, purified litmus solution (*cf.* pp. 67-68), or a solution of azolitmin (0·1 g. in 100 c.c.) is used. These should colour the paper a faint blue; if not, a trace of alkali may be added to the solution. For red paper, a trace of acid is of course added, and the neutral paper is prepared from a mixture of the two solutions. A sample should always be made and dried in order to be sure of the right colour, since a paper which is violet when wet becomes blue on drying. Neutral azolitmin paper is used for titrating weak acids.

Both yellow and red *methyl orange paper* is used. The yellow, prepared directly from methyl orange solution, should only be faintly coloured; it is employed for the detection of free mineral acids in the presence of weak acids, *e.g.*, free sulphuric acid in acetic acid, aluminium sulphate, zinc sulphate, etc., and in the titration of pyridine. The red paper, prepared with an acidified solution of the dye, can be used for the detection of bases, but it is not very sensitive.

Colourless *phenolphthalein paper* serves for the detection of free bases, but it is not as sensitive as red litmus paper. Red phenolphthalein paper is so readily acted upon by the carbon dioxide of the air and by light, that it is of no practical value.

Turmeric paper, prepared from the alcoholic extract of turmeric root, turns brown with alkalis (free or as carbonates), and with alkaline earths, but it is not very sensitive; its real use is for the detection of boric acid and salts of uranium.

Congo red paper, which is turned blue by alkalis and red by acids, is not very sensitive.

Lacmoid paper has, for most purposes, scarcely any advantage over litmus paper. It is used for the stronger organic acids and in testing for acid chromates, which in the presence of neutral chromate turn red lacmoid paper blue, and in the presence of free chromic acid turn the blue paper red, the colours making their appearance after the coloured chromate solution has been washed away. Red lacmoid paper has a very great tendency to turn blue, even with the moisture of the hand.

NORMAL SOLUTIONS

A large number of standard solutions are used in technical analysis; those employed only for special purposes are treated of in the sections in which their applications are discussed, the present section being restricted to a description of the standard solutions in general use, and which are employed in various branches of technical work.

General considerations.—Normal solutions are prepared either according to equivalents or according to units of weight of the substance to be estimated, or if they readily alter in strength on keeping, they are only approximately standardised and titrated anew for each series of experiments.

The first method is generally adopted. By "normal solution" in the narrower sense, that is an *N*/1 solution, is to be understood a solution of which one litre corresponds to a hydrogen equivalent, in grams, of the substance to be examined; $\frac{1}{2}$ normal, $\frac{1}{5}$ normal, and $\frac{1}{10}$ normal solutions (*N*/2, *N*/5, *N*/10) are equivalent to proportionately smaller amounts of the substance.

The ratio of the gram equivalents refers usually, but not always, also to the composition of the normal solution itself. Thus an *N*/1 hydrochloric acid solution contains 36·461 g. HCl per litre; an *N*/1 sulphuric acid which contains two replaceable hydrogen atoms = 49·04 g. H_2SO_4, and so on, but this is really only accidental. It is not a question of what the normal solution contains, but what it corresponds to. An *N*/1 hydrochloric acid solution must always correspond to a gram equivalent of a base, *e.g.* to 40·06 g. NaOH or $\frac{171}{2} = 85\cdot72$ g. $Ba(OH)_2$, which will, of course, be the case when it contains a gram equivalent HCl = 36·461 g. in the litre. But an *N*/10 potassium permanganate solution is not one which contains $\frac{1}{10}$th equivalent $KMnO_4 = \frac{158\cdot2}{10} = 15\cdot82$ g. per litre, but one which yields $\frac{1}{10}$th equivalent of oxygen $= \frac{16}{2 \times 10} = 0\cdot8$ g. O per litre. Since, according to the equation:—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O,$$

two molecules $KMnO_4$ yield $5 \times 16 = 80$ O, an *N*/10 permanganate solution must contain $2 \times 158\cdot2 \times \frac{0\cdot8}{80} = \frac{2 \times 158\cdot2}{100} = 3\cdot164$ g. of pure potassium permanganate, therefore only a fifth of the above amount of 15·82 g.

Normal solutions, prepared according to the chemical equivalents, have the merit of being applicable, without further calculation, to all cases in which they can be employed. Thus 1 c.c. of *N*/1 sodium hydroxide corresponds to 0·03646 g. HCl, or 0·04904 g. H_2SO_4, or 0·06305 g. HNO_3; 1 c.c. *N*/1 HCl, or *N*/1 H_2SO_4 corresponds to 0·03105 g. Na_2O, 0·04006 g. NaOH, 0·05305 g. Na_2CO_3, 0·05616 g. KOH, or 0·06915 g. K_2CO_3, etc. An *N*/10 permanganate solution corresponds to 0·005588 g. iron, or 0·006302 g. oxalic acid, etc. It is, therefore, customary to prepare such standard solutions as are applicable for a variety of purposes, in the ratio of their chemical equivalents.

An alternative method is preferable in special cases with solutions of this character. If, for example, it is only necessary to determine whether a commercial product is of a definite strength, it is more convenient, and saves time, to make up a volumetric solution to correspond to a simple quantity by weight of the substance in question, say, 1, 5, or 10 g. per litre.

This mode of preparing volumetric solutions is particularly suitable, and is to be generally recommended when the solution is employed exclusively or almost exclusively for the estimation of a simple substance, such as a silver nitrate solution for the determination of sodium chloride in products of the soda or salt industry, in Chili saltpetre, in drinking water, in boiler feed-water, in sulphates, etc.; or, conversely, when sodium chloride is used for estimating silver. In such cases there is no advantage whatever in making up solutions according to equivalents, as for example an $N/10$ silver nitrate solution, each c.c. of which corresponds to 0·0585 g. of sodium chloride, since a calculation, which cannot readily be made mentally, is then necessary for each titration; it is far preferable to prepare a solution containing, *e.g.*, 2·906 g. silver nitrate per litre, so that each c.c. then corresponds to 0·001 g. NaCl.

A third method is to make up the volumetric solution, not to correspond to chemical formulæ at all, but according to empirical tests. In the estimation of tanning materials with permanganate, according to Löwenthal's method, for example, it would be quite useless to weigh out an amount of permanganate yielding the oxygen requisite for oxidation, basing the calculation on the chemical formula of pure tannin; the amount of permanganate required is not the same under all circumstances, and cannot be calculated directly from the formula as with inorganic or simple organic substances, but depends upon how the estimation is carried out, on the temperature, and on the rate at which the oxidising substance is added; the titre of the permanganate solution, prepared by weighing out a simple, arbitrary quantity, must accordingly be determined empirically with an actual tannin, skin powder, etc.

STANDARD ACIDS

Hydrochloric acid, and for certain purposes *oxalic acid*, are the only acids really required for use as standard solutions; the latter cannot be used for alkalimetry. *Sulphuric acid* was formerly in general use as a standard acid, but it has been very largely displaced by hydrochloric acid, which has the threefold advantage that it is more generally applicable, as, for example, in the titration of the alkaline earths, that its strength can be controlled gravimetrically with silver nitrate much more accurately than that of sulphuric acid with barium chloride, and that it has a much greater avidity in the cold than sulphuric acid; further, as it is a monobasic acid, any disturbing influences such as are caused by the hydrolysis of acid sulphates are avoided.

There is no advantage to be gained by using sulphuric acid as a standard acid, and it can therefore be dispensed with altogether; it is prepared in exactly the same way as normal hydrochloric acid.

Normal nitric acid can also be substituted by hydrochloric acid, except for the estimation of chlorides, in an alkaline solution (for example, crude caustic soda) with silver nitrate, using potassium chromate as indicator; in this case an amount of standard nitric acid just sufficient to neutralise the alkali is added, this amount having been found from a previous titration with hydrochloric acid. For this purpose, however, a standardised nitric acid is not really necessary if methyl orange is used as indicator in the neutralisation; or, if an excess of acid has been added, it can be neutralised by a slight excess of sodium hydroxide or sodium carbonate, without disturbing the subsequent titration with silver nitrate.

Standard oxalic acid was brought forward by F. Mohr as a "basis of alkalimetry," but it has so many drawbacks that it is now but seldom employed, except for the standardisation of solutions, in which respect, however, it is much inferior to sodium carbonate. It is used for the preliminary standardisation of potassium permanganate solutions, and for estimating the "base" in Weldon mud.

Many different substances have been suggested as a *basis or standard for acidimetry and alkalimetry*, of which the following are the most important.

Sodium carbonate takes precedence of all the others, both on account of its extensive use and of its actual merit. It can be prepared and weighed out absolutely pure and free from water with the greatest ease, and can be very accurately titrated with hydrochloric acid and methyl orange, and, with proper precautions, with litmus or with phenolphthalein. "Chemically pure sodium carbonate," free from any appreciable amount of chloride, can be obtained commercially; it can also be readily prepared from sodium bicarbonate which has been freed from chloride and sulphate, if present, by washing with small amounts of distilled water. The sodium carbonate must be quite free from sodium oxide as well as from water.

If pure commercial sodium carbonate is used as a standard, it must dissolve in water to a perfectly clear solution, give no turbidity with silver nitrate after neutralisation with nitric acid, and no reaction for sulphates, after excess of hydrochloric acid has been added. In applying these tests a sufficient amount must be dissolved, say 2 to 3 g., and the solution sufficiently diluted, in order to avoid precipitation of barium chloride. A very slight opalescence with silver nitrate is often noticed, but it is easy to judge if an amount of chloride sufficient for quantitative estimation is present. If the sodium carbonate is pure, it is dried by heating in a platinum crucible, with frequent stirring, for twenty minutes, the temperature being so regulated that only the bottom of the crucible is red hot; it should not form into hard lumps during the heating, as this may indicate the formation of a little sodium oxide. The ignited substance is shaken into a well-stoppered

See Lunge, Z. angew. 1904, 231

weighing bottle whilst still warm, and kept in a desiccator; or the platinum crucible is allowed to cool in the desiccator and the several (three to five) portions for titration weighed directly into beakers, the crucible being kept covered during the weighings.

In order to be quite certain that the sodium carbonate has been ignited sufficiently but not too much, the crucible should preferably be heated in a sand bath to 270° to 300°, with continual stirring, until the weight is constant; half an hour is sufficient for this purpose, exclusive of the time required to attain the temperature. The sand is packed round the outside of the crucible to the same height as the sodium carbonate inside, and a thermometer is placed quite close to, or even in, the crucible. This method, which is quite as convenient as heating with the naked flame, is recommended by Lunge.

Sodium bicarbonate can be obtained commercially of a sufficient degree of purity for the preparation of the carbonate; it should be tested, as above, for the presence of insoluble impurities, chlorides and sulphates, of which the two latter can be removed by washing, owing to the slight solubility of the bicarbonate. The second equivalent of carbon dioxide and the water can then be driven off by heating in a platinum crucible, as in the case of sodium carbonate; but a more reliable result is attained by heating to a moderate temperature, which can be regulated. Lunge[1] has shown that the bicarbonate is completely converted into the carbonate by heating, for a few minutes, at 260° to 270°; if heated for from a half to one hour in a sand bath or in an air bath at a temperature not over 300°, the carbonate can be relied on as being free from bicarbonate, water, and sodium oxide.

Although sufficiently pure bicarbonate can readily be obtained commercially, yet it may at times be necessary to purify an impure product, so as to obtain a pure substance for standardising purposes. Reinitzer[2] gives the following method of purification. About 250 c.c. of distilled water is heated to 80° in a tall beaker (preferably of Jena glass) and the bicarbonate added, in small quantities at a time, till the solution is saturated, the liquid being continually stirred; during this process, part of the carbon dioxide is evolved, with effervescence. When nothing further dissolves, the solution is filtered through a pleated filter paper, preferably in a hot-water funnel, into a flask and cooled to 10° to 15°. In this way a considerable amount of a coarsely crystalline salt is thrown down, which is a mixture of bicarbonate and trona,[3] and which can be separated from the mother liquor by filtration through a funnel fitted with a platinum cone or with a loosely fitting glass stopper; it is preferable not to use a filter paper, so as to avoid contamination with fibres of paper. The mother liquor is pumped off and the substance

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[1] *Z. angew. Chem.*, 1897, **10**, 522.

[2] *Ibid.*, 1894, **7**, 551.

[3] $\frac{4}{3}$ Carbonate. Cf. *Z. angew. Chem.*, 1893, **6**, 446 and 573.

washed several times with small quantities of cold water, which are completely removed by suction after each addition. The salt is then transferred to a platinum crucible, which is heated to such a temperature that it is just visibly red hot in daylight; after cooling, it is powdered and again dried. If this method is employed, it is difficult, when dealing with large quantities, to avoid overheating some portions, and thus producing traces of sodium oxide. It is therefore better simply to dry the salt thoroughly, grind and mix together, and then to heat the small quantities to be employed in standardising, in a sand bath or air bath, to a temperature not exceeding 300°, as above.

For standardising or controlling the strength of a normal acid, the corresponding quantities of sodium carbonate must always be weighed out separately; the plan of preparing a normal sodium carbonate solution containing say 53 g. to the litre and withdrawing aliquot portions for the different estimations, is unsatisfactory. Errors in measuring, in the emptying of pipettes, etc., cannot be avoided, even when standardised apparatus is employed, and the inaccuracy arising from these causes is much greater than errors of weighing.

The possibility of preparing sodium carbonate quite free from moisture and from sodium hydroxide has, from time to time, been questioned by various investigators.[1] Lunge[2] has, however, shown that the product obtained by the method of ignition given above is quite free from moisture, and that the quantity of sodium hydroxide formed is negligible for all ordinary analytical work; in a special experiment to test this point, he found only 0·004 per cent. of the hydroxide in a sample of carbonate dried at 270° to 300°.

Sörensen[3] has recommended the use of *sodium oxalate* as the basis for alkalimetry instead of sodium carbonate; it has the advantage of being applicable also as a standard for oxidation methods of volumetric analysis. The salt can readily be obtained free from water of crystallisation, according to Sörensen, and is not hygroscopic. As prepared according to his directions, by Kahlbaum, by precipitation with alcohol and drying at 240°, it may be employed for standardising purposes, either directly or after a few hours' heating in the steam oven. An accurately weighed quantity of the salt is carefully heated, for a quarter to half an hour, in a covered platinum crucible, over a small gas flame, supported in a hole in an asbestos card, so as to avoid contamination by sulphur compounds from combustion, or over a spirit lamp,[4] until the sodium carbonate formed just begins to fuse; towards the end of the operation

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[1] *Cf.* C. L. Higgins, *J. Soc. Chem. Ind.*, 1900, **19**, 958; Sörensen and Andersen, *Z. anal. Chem.*, 1905, **44**, 156; B. North and W. Blakey, *J. Soc. Chem. Ind.*, 1905, **24**, 396; Sebelien, *Chem. Zeit.*, 1905, **29**, 638.

[2] *Z. angew. Chem.*, 1904, **17**, 231; 1905, **18**, 1520.

[3] *Z. anal. Chem.*, 1897, **36**, 639; 1903, **42**, 333; 1905, **44**, 156.

[4] *Cf.* Lunge, *Z. angew. Chem.*, 1905, **18**, 1520.

the lid is moved aside so as to cover about one-half of the crucible, to promote the complete combustion of the carbon formed. A mixture of sodium carbonate, containing a little sodium hydroxide, is thus formed, which is not weighed, but transferred along with the crucible to a tall beaker, moistened with water, treated with an excess of the acid to be standardised and warmed on the water bath; the solution is then poured into a conical flask, the crucible and cover and the beaker rinsed out, ten drops of a solution of 0·5 g. phenolphthalein in 50 c.c. alcohol + 50 c.c. water added and boiled, till the carbon dioxide is completely expelled, in a current of air freed from carbon dioxide, cooled in cold water, and the excess of acid titrated back with $N/10$ sodium hydroxide. The equivalent of sodium oxalate is $\frac{134·1}{2} = 67·05$, so that 10 c.c. of an $N/10$ acid correspond to 0·06705 g. of sodium oxalate; or 0·1 g. of the salt = 14·91 c.c. of an $N/10$ acid. In a subsequent paper,[1] Sörensen gives accurate directions for the examination of commercial "pure" sodium oxalate, for impurities.

Sörensen's investigations were carried out with great care, and they show that very good results are obtainable with sodium oxalate, as a basis for alkalimetry. Whether the ignition of the oxalate with complete combustion of the carbon (regarded by Sörensen himself as absolutely necessary) can be performed without loss by those without special experience in the method, requires confirmation. The examination of the substance as regards absolute purity is more troublesome and tedious than in the case of sodium carbonate, and this is true of the whole process, even if the titration is not carried out with phenolphthalein in boiling solution as above, which is quite unnecessary, but with methyl orange in the cold.[2] There is, therefore, no reason for giving sodium oxalate the preference over sodium carbonate, but it can be advantageously used as a control in doubtful cases.

To prepare an $N/1$ hydrochloric acid solution, pure hydrochloric acid is diluted to a specific gravity of about 1·020, so as to obtain a preliminary acid somewhat over the normal strength (36·46 g. HCl per litre). This acid is then titrated against a freshly ignited sample of sodium carbonate. If w is the weight of carbonate neutralised by x c.c. of acid, $x = \frac{w}{0·05305}$ will correspond to a normal solution. From this formula the number of c.c. of normal acid that would be required is calculated; this number, y, is therefore $= \frac{w}{0·05305}$, and x will be smaller than y if the preliminary acid is too strong, which is generally the case. In order to find out how much the "preliminary" acid must be diluted

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[1] *Z. anal. Chem.*, 1903, **42**, 512.

[2] *Cf.* Lunge, *Z. angew. Chem.*, 1905, **18**, 1520.

to obtain a normal solution, let $u = \frac{1000x}{y}$; u is then the number of c.c. of the preliminary acid which has to be made up to 1000 c.c. with water to obtain a normal acid.

If normal sodium hydroxide is available, it may be used in an exactly analogous way to titrate the "preliminary" acid and to prepare a normal solution.

The diluted acid is then titrated against new samples of freshly ignited sodium carbonate as a check, that is, to ascertain if $x=y$. A further control, by determining the proportion of chlorine with silver nitrate, is also very desirable; 10 c.c. of the acid (=0·3646 g. HCl) should give 1·435 g. AgCl.

Since 50 c.c. of $N/1$ acid, the capacity of an ordinary burette, corresponds to a weight of 2·652 g. of sodium carbonate, from 2·0 g. to 2·5 g. should be weighed out for each titration, so as to reduce the error in reading the burette, as far as possible. If only 20 c.c. of acid are used for the titration, the effect of the error in reading is double that for 40 c.c., and if more than 50 c.c. is needed, so that the burette has to be refilled, four instead of two readings are necessary, so that the degree of accuracy is also lessened. The use of 100 c.c. burettes of the ordinary form, in order to avoid the four readings, is also disadvantageous, because they can only be graduated into fifths of a c.c. with accuracy, and the error in reading is thus double that with a 50 c.c. burette graduated in tenths. If, however, a great many analyses requiring the use of more than 50 c.c. of acid for each titration have to be made, burettes with bulbs, constructed on the principle of Lunge's bulb nitrometer, may be employed, in which the accurate graduations begin at 60 or 70 c.c.

In order to interpret the experimental results clearly, a coefficient for the normal acid should be calculated from each observation, by finding the amount of acid theoretically necessary to neutralise the weighed quantity of sodium carbonate and dividing this by the number of c.c. actually required; the quotient gives the number with which the results of the titration have to be multiplied to find the amount of sodium carbonate actually present. Suppose, for example, that 2·500 g. of sodium carbonate have been weighed out, and that this amount neutralises 47·00 c.c. of acid; if the acid had been actually normal, $\frac{2 \cdot 500}{0 \cdot 05305} = 47 \cdot 13$ c.c. would have been required. The acid is, therefore, slightly too strong, and the readings must be multiplied by $\frac{47 \cdot 13}{47 \cdot 00} = 1 \cdot 0028$ to correspond to normal acid.

All normal solutions should be prepared at 15°, and a correction must be applied as detailed on p. 45, if they are subsequently employed at a temperature differing by more than 1° or 2° from 15°.

In order to be able to rely on the correctness of a normal acid, at least three, but preferably four, experiments should be made, and the greatest deviations from the coefficient, calculated as above, should not exceed 0·0010, so that the mean of the results has a maximum error of ±0·0005. A skilled worker can get more accurate results, but it is not easy to get within the half of the above error, that is, an error of ±0·025 per cent. and ±0·01 per cent., which may be regarded as the greatest obtainable accuracy, can only be attained by taking very special precautions, making the readings with a cathetometer, etc. Since small errors may be introduced each time the normal solution is used, the second decimal place per cent. is always uncertain in alkalimetric and acidimetric observations, and even the correctness of the first decimal place, that is one-thousandth of the total amount, is only to be depended on when very great care is taken. It is, therefore, absurd to calculate out analyses of this kind to more than two decimal places per cent.

In scientific laboratories it is usual to prepare a volumetric solution of approximate accuracy and to correct the readings by means of a coefficient, determined as above. In technical laboratories, on the other hand, where large amounts of standard solutions are made up at once, the use of a coefficient involves loss of time and may give rise to error; it is, therefore, preferable to adjust the solutions so that no correction is required. If the coefficient does not exceed ±0·002, this deviation from a normal solution can, in most cases, be neglected.

Of other substances which have been suggested for the standardising of normal acids and alkalis, the following are the most important.[1]

Grandeau,[2] and subsequently Pincus[3] and Fresenius,[4] suggested the use of *calcspar* (Iceland spar), which they regard as chemically pure calcium carbonate, but this is not always the case. Thiele and Richter[5] found deviations of 0·2 per cent. from the true value, with this substance.

Hartley[6] and Neitzel[7] have made use of metallic *sodium*.

Borax is recommended by Salzer,[8] Rimbach and Worms,[9] Richmond,[10] Buchanan,[11] and Perman and John.[12]

Ammonium chloride has been suggested by Reinitzer,[13] and by Seyda and Weinig,[14] and *ammonium sulphate* by Knublauch.[15]

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[1] Many of the following references are taken from a paper by Vanino and Seitter, *Z. anal. Chem.*, 1902, **41**, 141, which contains a fairly complete summary of the literature on volumetric solutions and substances used in standardising them. *Cf.* also B. North and W. Blakey, *J. Soc. Chem. Ind.*, 1905, **24**, 396.

[2] *Z. anal. Chem.*, 1863, **2**, 426.

[3] *Ibid.*, 1863, **2**, 426.

[4] *Quantitative Analysis*, 7th edition, vol. ii., p. 194.

[5] *Z. angew. Chem.*, 1900, **13**, 486.

[6] *Z. anal. Chem.*, 1873, **12**, 89.

[7] *Ibid.*, 1893, **32**, 122.

[8] *Ibid.*, 1893, **32**, 449.

[9] *Ibid.*, 1896, **35**, 338; 1897, **36**, 688.

[10] *Chem. News*, 1895, **72**, 5.

[11] *J. Soc. Chem. Ind.*, 1904, **23**, 1093.

[12] *Chem. News*, 1895, **71**, 296.

[13] *Z. anal. Chem.*, 1895, **34**, 577; 1900, **39**, 458.

[14] *Z. angew. Chem.*, 1892, **5**, 204.

[15] *Z. anal. Chem.*, 1882, **21**, 165.

An *iodometric method*, based on the reaction :—

$$5KI + KIO_3 + 6HCl = 6I + 3H_2O + 6KCl,$$

is described by Mohr, Kjehdahl,[1] Gröger,[2] and Fessel.[3] v. Than[4] proposed *potassium bi-iodate*, which is also recommended by Meineke.[5] Riegler[6] has suggested pure *iodic acid*. All the iodometric methods for preparing normal acids and alkalis are indirect, and the sum of the small unavoidable errors may easily exceed the permissible limit stated on page 88. The basis of iodimetry is not more certain than that of acidimetry, if pure sodium carbonate is used as the standard, but rather the contrary, so that acidimetry may justifiably be employed as a basis for iodimetry rather than the reverse (*cf.* p. 117).

The iodometric method is recommended by Petersen[7] for determining the amount of acid in coloured plant extracts, roots, beer, etc.

Morse and Chambers[8] base a method of standardisation on the decomposition of neutral *hydrogen peroxide* by potassium permanganate, according to the equation :—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

In this reaction the volume of gas evolved may, of course, also be measured. Another method, involving measurement of a gas, in which potassium iodide, potassium iodate, sodium hydroxide, and hydrogen peroxide are employed, has been proposed by A. Baumann.[9]

Hart and Croasdale[10] and Kohn[11] have proposed the electrolysis of *copper sulphate* as a basis for acidimetry. The advantage of this proposal lies in the fact that it is dependent only upon the ratio of copper to sulphuric acid. The copper sulphate itself need not be weighed, and therefore the difficulty of obtaining a substance, which can be dried without decomposition or without loss of water of crystallisation, is avoided. It is only necessary that the sulphate is free from metals other than copper, and this degree of purity is effected by two recrystallisations of the commercial salt, a little nitric acid being added in the first recrystallisation to oxidise any ferrous sulphate present. From 1 to 2 g. of copper sulphate is electrolysed in aqueous solution, and the weight of sulphuric acid formed determined from the weight of the equivalent of copper deposited. The method serves only as a basis from which the strength of other solutions may be determined, but not for preparing actual standard solutions for use, as there is an obvious limitation to the quantity of solution that can be conveniently prepared in this way. Dauvé[12] states that good

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[1] *Z. anal. Chem.*, 1883, **22**, 327.

[2] *Z. angew. Chem.*, 1890, **3**, 353 and 385.

[3] *Z. anorg. Chem.*, 1899, **23**, 67 ; **38**, 1904, 449.

[4] *Annalen*, 1891, **261**, 358.

[5] *Chem. Zeit.*, 1895, **19**, 2.

[6] *Z. anal. Chem.*, 1896, **35**, 308 ; 1899, **38**, 250.

[7] *Z. anal. Chem.*, 1903, **42**, 308.

[8] *Ibid.*, 1898, **37**, 183.

[9] *Ibid.*, 1892, **31**, 450.

[10] *J. anal. Chem.*, 1890, **4**, 424 ; 1892, **6**, 421.

[11] *J. Soc. Chem. Ina.*, 1900, **19**, 962.

[12] *J. Pharm. Chem.*, 1902, **16** [2], 65.

results cannot be obtained by this method, because if no free acid is present, the deposited copper does not adhere to the electrode and contains suboxide of copper, but no experiments are given to support this conclusion. Meade[1] has described the preparation of standard sulphuric acid, and indirectly of standard hydrochloric and nitric acids, by the electrolysis of copper sulphate.

North and Blakey[2] recommend sodium bicarbonate for fixing the strength of standard acids, but according to Lunge[3] it is not reliable.

Normal hydrochloric acid can of course be prepared and checked gravimetrically, by precipitation with silver nitrate. Lunge finds that with careful working, the results by this method agree with those obtained by the use of sodium carbonate to within 0·05 per cent., sometimes even to within 0·02 per cent.; he does not regard this gravimetric method as more accurate than standardisation with pure sodium carbonate.

It is much more difficult to attain the same degree of accuracy with normal sulphuric acid by precipitation with barium chloride, owing to the well known difficulty of obtaining absolutely pure barium sulphate.

Several authors have recommended evaporating down the acids with ammonia, and weighing the ammonium salt formed.

Moody[4] has suggested the preparation of normal hydrochloric acid, by passing hydrochloric acid gas into a known weight of water, and determining the increase in weight. The method has since been studied and improved by Higgins;[5] very accurate results can be obtained, but somewhat special apparatus is required which is hardly suitable for technical work. Both Roth[6] and Raschig[7] have also described this method.

A. Marshall[8] recommends the preparation of normal sulphuric acid on the basis of its specific gravity. This proposal has been extended to hydrochloric acid by Küster and Siedler,[9] but the examples given show too great deviations from the actual strength, even in cases regarded by them as correct up to 0·5 per cent., to allow of the recommendation of the method, for accurate work. In a later communication,[10] Küster and Münch state that the method is correct to within ±0·0001 of the sp. gr. Tables of specific gravities of sulphuric acid and of hydrochloric acid, between the limits of $N/10$ and $N/1$ solutions, have

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[1] *J. Amer. Chem. Soc.*, 1901, **23**, 12 and 343.

[2] *J. Soc. Chem. Ind.*, 1905, **24**, 396.

[3] *Z. angew. Chem.*, 1905, **18**, 1520.

[4] *Chem Soc.*, 1897, **73**, 658.

[5] *J. Soc. Chem. Ind.*, 1900, **19**, 958.

[6] *Z. angew. Chem.*, 1904, **17**, 710; *J. Soc. Chem. Ind.*, 1904, **23**, 837.

[7] *Z. angew. Chem.*, 1904, **17**, 577.

[8] *J. Soc. Chem. Ind.*, 1900, **19**, 4; 1902, **21**, 1511.

[9] *Chem. Zeit.*, 1902, **26**, 1055; *Ber.*, 1905, **38**, 150.

[10] *Ber.*, 1905, **38**, 150; *Z. anrg. Chem.*, 1905, **43**, 373.

also been prepared by Worden and Motion;[1] such tables may very well be used for the approximate adjustment of volumetric solutions.

Quincke[2] has proposed a method, depending upon the measurement of oxygen evolved from potassium ferrocyanide and alkaline hydrogen peroxide.

There are several methods, in which an acid substance is taken as the basis, by means of which an alkaline solution is standardised and the latter then employed for standardising a normal acid.

The most important of the compounds used in this way is *oxalic acid*, the value of which, as a basis for acidimetry, has been advocated by Mohr. It is, however, very difficult to prepare oxalic acid quite pure, and with the definite proportion of water corresponding to the formula $H_2C_2O_4.2H_2O$. This difficulty is by no means overcome by Hampe's suggestion[3] to use the extremely hygroscopic anhydrous acid, which sublimes at 100°, instead of crystallised oxalic acid. Of the numerous methods proposed for the preparation of pure oxalic acid, that of C. Winkler is most largely used.[4] 500 g. of commercial oxalic acid are dissolved in an equal weight of boiling hydrochloric acid of sp. g. 1·07, in a porcelain basin, the solution placed in ice water and allowed to crystallise, with continual stirring; the finely crystalline mass is transferred to a funnel, provided with a plug of glass wool, allowed to drain, and washed several times with hydrochloric acid. It is then redissolved in pure, boiling hydrochloric acid, again cooled with continual stirring, the crystals filtered off, washed with a little water and recrystallised by dissolving in just the requisite amount of boiling water. The finely crystalline mass thus obtained is again washed and the whole treatment is repeated two or three times. The final product is left to dry in a cool place, the drying material being repeatedly changed. Thus prepared, it is free from chlorine and mineral matter, but still contains enclosed liquid, and must therefore be dehydrated before use. This is best effected by drying for five to six hours at 60°, as oxalic acid volatilises to a considerable extent at 100°. The dry acid having the formula $H_2C_2O_4$, must naturally be kept in tightly closed bottles; when it is to be employed for standardising purposes, about 0·2 g. is weighed out into each of several weighing tubes, again dried for several hours at 60° to 80°, allowed to cool in the closed tubes, and then accurately weighed.

This somewhat troublesome method of purification is likely to prove too tedious for technical work, and the method possesses no advantage over the use of pure sodium carbonate. Winkler recommends it only for standardising purposes, and not for the preparation of normal oxalic acid. To carry out the method, a normal alkali is first standardised with

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[1] *J. Soc. Chem. Ind.*, 1905, **24**, 178.

[2] *Z. anal. Chem.*, 1892, **31**, 1.

[3] *Chem. Zeit.*, 1883, **7**, 73 and 106.

[4] *Uebungen in der Massanalyse*, 3rd edition, p. 69.

the oxalic acid and then used for adjusting the strength of the normal acid; the method is, therefore, indirect, and accordingly liable to small unavoidable errors which do not arise in direct standardisation. The normal alkali used in the titration must either be free from carbon dioxide, or the solution must be boiled, allowed to cool, and the titration completed. Instead of an alkali hydroxide, barium hydroxide may be employed, but the adjusting of the latter solution, so as to contain an exact equivalent, is difficult (cf. *infra*).

Instead of oxalic acid, its acid salt, potassium tetroxalate, is regarded by many as a more reliable basis for alkalimetry, as also for the titration of potassium permanganate. The crystallised salt has the formula $KHC_2O_4.H_2C_2O_4.2H_2O$; its employment was first suggested by Kraut,[1] and subsequently recommended by Ulbricht and Meissl,[2] and by Meineke,[3] whilst Wells,[4] Hinmann,[5] and Dupré and Kupffer[6] have criticised its value adversely. It can be used either with litmus or preferably with phenolphthalein as indicator; as in the case of free oxalic acid, the presence of carbon dioxide in the alkali must be taken into consideration. The tetroxalate has recently been again strongly recommended by J. Wagner,[7] who frees it from moisture by pressing between blotting paper, instead of by standing over sulphuric acid, as recommended by Meineke, and employs it in the air-dried state. It can be obtained, free from the dioxalate which it is apt to contain, by dissolving one gram-molecule of neutral oxalate in water and adding it to a solution of rather more than three molecules of oxalic acid, in such a way that excess of the latter is always present; the solution is warmed for an hour on the water bath, and the product recrystallised. The tetroxalate is then used for standardising barium hydroxide with phenolphthalein as indicator, and the strength of the normal acid adjusted from the hydroxide.[8] The same method is recommended by Kühling.[9] Lunge[10] states that, as the result of a large number of experiments, he has not succeeded in obtaining potassium tetroxalate with a constant proportion of water corresponding to the formula given above, and he therefore does not concur in recommending it in place of sodium carbonate as a basis for alkalimetry, although it may quite well be employed for the standardisation of potassium permanganate, *via* sodium carbonate, hydrochloric acid, and barium hydroxide.

Objection must be made on principle to standardisation with oxalic acid, potassium tetroxalate and all other substances, such as potassium

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[1] *Annalen*, 1863, **126**, 629.

[2] *Z. anal. Chem.*, 1887, **26**, 350.

[3] *Chem. Zeit.*, 1895, **19**, 2.

[4] *Z. anal. Chem.*, 1893, **32**, 453.

[5] *Ibid.*, 1894, **33**, 456.

[6] *Z. angew. Chem.*, 1902, **15**, 352.

[7] *Proc. 5th International Congress for Applied Chemistry*, 1903.

[8] J. Wagner, private communication.

[9] *Z. angew. Chem.*, 1903, **16**, 1030; *Chem. Zeit.*, 1904, **28**, 596 and 612.

[10] *Z. angew. Chem.*, 1904, **17**, 227; *Chem. Zeit.*, 1904, **28**, 701.

bi-iodate and cream of tartar, with which phenolphthalein is used as indicator, when the normal solutions are subsequently used with methyl orange (*cf.* p. 60).

Potassium bi-iodate has been recommended as a basis for the direct adjustment of normal sodium carbonate by Meineke[1] and by E. Crato.[2] According to Lunge,[3] iodic acid behaves, towards methyl orange, as a rather weaker acid than hydrochloric acid and similar acids; this is naturally not the case with phenolphthalein, but still the results are not very accurate, nor is it possible to establish the absolute purity of the substance readily and quickly by qualitative analysis, as in the case of sodium carbonate. J. Wagner also finds[4] that the commercial "chemically pure" bi-iodate often does not correspond to the formula $KH(IO_3)_2$, and that it cannot be satisfactorily dried by the method recommended by Meineke. There is accordingly no reason for using this salt in preference to sodium carbonate as a basis for alkalimetry, either directly or indirectly.

Potassium hydrogen tartrate has been recommended as a standard by Bornträger;[5] it appears to be used at Italian experimental stations. The weak acidic character of tartaric acid and the consequent decrease in the sharpness of the transition tints of the indicator, is an obvious objection to its use, and it has no advantages over sodium carbonate.

Potassium bichromate has been suggested by Richter[6] as a substance which can readily be obtained pure, but even if this be so, the weak acidic character of chromic acid and the transition in colour from one tint of yellow to one of a more reddish hue, are clearly unfavourable to its use in alkalimetry.

The Strength of Normal Acids.

In works, $N/1$ acid is used for controlling working processes and for many laboratory purposes; the change of colour of the indicator with acid of this strength is very sharp, under all circumstances. Its use necessitates taking a correspondingly larger amount of substance for analysis, and in practice, a sufficient degree of accuracy is attainable, with less carefully calibrated weights and measuring vessels, than are used for other work. It is, however, often necessary to work more accurately, and there is then the choice of $\frac{1}{2}$, $\frac{1}{5}$, or $\frac{1}{10}$ N acid. These are most readily prepared by dilution of the normal acid; the strength of the diluted acid must always be checked as directed on page 87, for which purpose 1·000 to 1·250 g. of sodium carbonate is weighed out for the $N/2$ acid, 0·4 to 0·5 g. for the $N/5$ acid, and 0·2 to 0·25 g. for the $N/10$ acid.

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[1] *Chem. Zeit.*, 1895, **19**, 2.

[2] *Massanalytische Tafel.*

[3] *Z. angew. Chem.*, 1904, **17**, 225.

[4] *Massanalytische Studien*, p. 60.

[5] *Chem. Zeit.*, 1881, **5**, 519; *Z. anal. Chem.*, 1886, **25**, 333; 1892, **31**, 56; 1894, **33**, 713.

[6] *Z. anal. Chem.*, 1882, **21**, 205; *cf.* also, *Z. anorg. Chem.*, 1893, **3**, 84.

It is undesirable to have too many normal solutions in use, and usually one other acid besides the normal acid suffices; $N/5$ acid is the best strength for the dilute acid. Very little is gained by using $N/2$ acid instead of the normal, and $N/10$ acid is too dilute to use as the weaker solution; at least two drops of it are required to bring about a sharp change of colour, so that it is really not more accurate than $N/5$ acid, only one drop of which is required to effect the same result. Titrations to within one drop of an $N/5$ solution (0·02 to 0·03 c.c) are as near as can be relied upon, taking into account the lack of sensitiveness of many indicators and other sources of inaccuracy.

In works, a large quantity of normal acid is usually prepared at once, say 50 to 60 litres, the capacity of an acid carboy. For laboratory use it must, of course, be transferred to smaller vessels, such as stoppered bottles, holding at most 5 litres; this is preferably done as soon as the acid has been standardised. If, however, a sufficient number of smaller vessels is not available, or if there is no room for them, so that the carboy has to be emptied gradually, care must be taken to stopper it well, and to shake thoroughly before use (*cf.* p. 52). The smaller bottles must also be well shaken once a day before use, since water may evaporate and condense in the upper empty part of the vessel.

The equivalent of 1 c.c. of $\frac{1}{1}$, $\frac{1}{2}$, $\frac{1}{5}$, and $\frac{1}{10}$ N acids, in grams of the substance to be estimated, is given in the following table:—

	$N/1$	$N/2$	$N/5$	$N/10$
Potassium Hydroxide	0·05616	0·02808	0·01123	0·005616
Potassium Oxide	0·04715	0·02357	0·00943	0·004715
Potassium Carbonate	0·06915	0·03457	0·01383	0·006915
Sodium Hydroxide	0·04003	0·020015	0·00801	0·004003
Sodium Oxide	0·03105	0·01552	0·00621	0·003105
Sodium Carbonate	0·05305	0·02652	0·01061	0·005305
Barium Hydroxide	0·08572	0·04286	0·01714	0·008572
Barium Carbonate	0·09872	0·04936	0·01974	0·009872
Strontium Hydroxide	0·06082	0·03041	0·01216	0·006082
Strontium Carbonate	0·07382	0·03691	0·014764	0·007382
Calcium Hydroxide	0·03707	0·01853	0·007414	0·003707
Calcium Oxide	0·02806	0·01403	0·005613	0·002806
Calcium Carbonate	0·05006	0·02503	0·010013	0·005006
Magnesium Oxide	0·02018	0·01009	0·004036	0·002018
Magnesium Carbonate	0·04218	0·02109	0·008436	0·004218

Normal Oxalic Acid.

Oxalic acid is quite superfluous for alkalimetry, but it is nevertheless still used by some chemists, and is required for a few other purposes, such as the examination of Weldon mud. It cannot be employed with methyl orange as indicator, and even for the estimation of the hydroxides of the alkaline earths, in the presence of their carbonates, it can be completely replaced by hydrochloric acid.[1]

It can be readily prepared by dissolving 63·025 g. of chemically pure oxalic acid in one litre for the normal acid, and correspondingly smaller amounts for the weaker acids; since the preparation of absolutely pure and dry oxalic acid, according to the method detailed on p. 91, is so troublesome, even C. Winkler, who holds to this acid as the basis of alkalimetry, recommends that normal oxalic acid for use should be prepared of approximate strength from the ordinary "pure" acid, and the strength determined by titration with accurate normal alkali.

Only very weak acidic indicators, such as litmus and still better phenolphthalein, can be used with oxalic acid. The solutions do not keep well and decrease in stability with the degree of dilution. They decompose gradually even in closed vessels and when kept in the dark, but more rapidly when exposed to light. The more concentrated solutions, including the $N/1$ acid, are, however, fairly stable; if sterilised, they can be kept in the dark for some years without alteration in strength.[2] Very dilute solutions such as the $N/100$ acid, used in water analysis for the determination of "organic matter," keep only for a very short time, and must be prepared fresh on each occasion. The strength can, of course, readily be determined, at any time, by titration with sodium hydroxide, using litmus or phenolphthalein as indicator; in order to obtain accurate results, the solution should be boiled with a slight excess of sodium hydroxide, cooled quickly, and titrated back in the cold, in order to avoid error, owing to the presence of sodium carbonate in the hydroxide.

Standard Alkalis

The hydroxides of sodium, potassium, ammonium, and barium are employed as standard alkalis; of these, the first is most largely used. The only reason for using the more expensive potassium hydroxide is that it has rather less action on glass; this is true for solutions of the same percentage composition, but apparently not for solutions of the same molecular concentration.[3] Mohr found that burettes filled with sodium hydroxide sometimes cracked longitudinally, which was not the case when potassium hydroxide was used; this is, however, of so infrequent occurrence, that it cannot be regarded as a reason for limiting the use of sodium hydroxide.

Ammonium hydroxide has been recommended as a standard alkali because it does not readily absorb carbon dioxide from the air and has

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[1] Küster, *Z. anorg. Chem.*, 1898, **18**, 127; Lunge, *Z. angew. Chem.*, 1897, **10**, 41.

[2] H. Beck, *Inaugural Dissertation*, Jena, 1902.

[3] Lunge and Millberg, *Z. angew. Chem.*, 1897, **10**, 398.

no action on glass. These advantages, the first of which is only relative, are, however, counterbalanced by the tendency of the solutions to give up ammonia. Even $N/2$ and $N/5$ solutions alter in strength so rapidly that they cannot be used for any length of time without control; such solutions should not be allowed to stand, even for a short time, in burettes which are not thoroughly shut off from the air.

Barium hydroxide, which absorbs carbon dioxide from the air, giving a precipitate of the carbonate, can only be used when all the usual precautions are taken to obviate this source of error. It is difficult to prepare a normal solution and still more difficult to keep its strength unaltered, so that a correction factor has always to be used. It is only in certain cases that the advantages of barium hydroxide are sufficient to counterbalance these drawbacks, as, for example, in the titration of weak acids with phenolphthalein, since, unlike the hydroxides of potassium and sodium, it can readily be obtained free from carbon dioxide. When this is of no advantage, as in all cases in which methyl orange is used as indicator, nothing is gained by its use.

Sodium hydroxide.—In technical laboratories and even for most scientific purposes, the commercial white caustic soda may be used directly for preparing this solution, since the impurities usually present, such as chloride, sulphate, silicate, and aluminate, very seldom affect the result. Sodium hydroxide in sticks, purified by alcohol, answers all requirements. The expensive product prepared from metallic sodium contains not only sodium carbonate, but sometimes gives a flocculent residue on solution. A similar residue is often obtained when ordinary caustic soda is used, and a sample should therefore be selected which dissolves in water to a clear solution; otherwise the solution must be allowed to settle and the clear liquid decanted.

To prepare normal sodium hydroxide, clear transparent lumps of the best white commercial caustic soda are picked out, any opaque parts on the surface scraped off, and 50 g. weighed out for each litre. It is then dissolved in water, made up to the litre at 15°, and 50 c.c. of this provisional solution titrated with accurately normal hydrochloric acid, using methyl orange as indicator, till the brownish transition tint appears (p. 62). If n c.c. of acid are used, the number of c.c. of the preliminary alkali, which must be diluted to a litre, with pure water, to obtain accurately normal sodium hydroxide, is $\frac{50 \times 1000}{n}$.

The solution must, of course, be titrated again to check its accuracy; weaker solutions are similarly prepared.

Bousfield and Lowry[1] have shown that standard solutions of sodium hydroxide can be prepared from metallic sodium. Küster[2] has also

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[1] *Phil. Trans.*, 1905, **204**, 253.

[2] *Z. anorg. Chem.*, 1904, **41**, 472. *J. Soc. Chem. Ind.*, 1904, **23**, 1027; 1906, **25**, 982.

described a method for the preparation of pure sodium hydroxide solutions from the metal.

As is well known, sodium hydroxide solutions should not be kept in bottles with ground-glass stoppers, as these easily become fixed in the neck of the bottle. This difficulty is to some extent overcome by greasing the stoppers with a little paraffin or vaseline, or by tying a thread round the stopper, or by covering it with a piece of wide rubber tubing; a rubber stopper may also be used. Corks cannot be used, as they soon decay and pieces fall into the solution.

It is not advisable to prepare very large amounts of sodium hydroxide at once as a stock solution, because it slowly attacks the glass and alters a little in strength. In order to obtain accurate results when litmus or phenolphthalein are used as indicators, the hydroxide must be prepared free from carbon dioxide, and when in use, especially in the burette, must be carefully guarded from contact with this gas.

To effect this, it has been suggested that the sodium or potassium hydroxide should be boiled with milk of lime, till a filtered sample evolves no carbon dioxide when poured into dilute hydrochloric acid. This mode of procedure is, however, insufficient to remove the carbonate completely. The method suggested by Küster,[1] to dissolve sodium in boiling alcohol, displace the alcohol by water, free from carbon dioxide, and dilute with the latter to normal strength, would certainly give more satisfactory results, but the method is inconvenient and expensive, and is not likely to be used in technical laboratories. Moreover, Lunge found that solutions prepared in this way, with all possible precautions, still contained considerable amounts of carbon dioxide.

Küster and Grüters[2] recommend that barium hydroxide should always be used for accurate determinations with phenolphthalein, because potassium and sodium hydroxides give uncertain results, owing to the variable amounts of contained carbonate.

There is, further, no object in preparing an alkali hydroxide solution free from carbon dioxide, unless its re-absorption from the air is carefully guarded against, when in use. To effect this, the solutions should always be prepared and diluted with boiled, carbon dioxide-free water, the titration should be made, as far as possible, without access of air, and the burette and supply-vessel should be guarded against the absorption of the gas. The method generally adopted to protect the solution is to provide the supply-bottle with a stopper with three holes; in one is placed a soda-lime tube open to the air, the second is connected with the top of the burette, and a syphon tube, reaching to the bottom of the bottle, is placed in the third hole and connected by means of a T-piece with the lower part of the burette, above the pinch-cock. There are con-

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[1] *Z. anorg. Chem.*, 1897, **13**, 134; *cf.* Treadwell, *Analytical Chemistry*, vol. ii., p. 441.

[2] *Ibid.*, 1903, **35**, 459.

siderable objections to this arrangement, however, since although the carbon dioxide is excluded, it renders the daily shaking of the supply-bottle, which is absolutely necessary, owing to evaporation or condensation of water in the upper part of the latter, difficult or impossible. If the connections, as is preferable in other cases, are made, as far as possible, of glass, and are therefore rigid, shaking is out of the question; if rubber tubing is used instead, the alkali becomes contaminated, especially with sulphur, by prolonged contact. It is therefore preferable to close both burette and stock-bottle with a soda-lime tube and not to connect them, but to fill the burette at the top in the usual way, after shaking the bottle; no appreciable error arises from the momentary contact of the alkali with the air, certainly less than when the burette and flask are rigidly connected. Some such mode of connection as that described above is, however, essential in using barium hydroxide solutions.

Glaser[1] and others contend that the errors due to the small quantities of carbonate contained in solutions of the alkali hydroxides and to the carbon dioxide absorbed from the air during titration, are practically negligible when litmus or phenolphthalein are used as indicators, and may be disregarded. Experiments by Lunge[2] and by Raschig,[3] however, show definitely that this is not the case. In a series of determinations by the former, 25 c.c. of $N/5$ hydrochloric acid required exactly 25 c.c. of $N/5$ sodium hydroxide, prepared from metallic sodium and using methyl orange as indicator, in each of three independent determinations; in six determinations with phenolphthalein, titrated cold, the minimum value was 25·54 c.c., the maximum 25·63 c.c., an average of 25·59 c.c., or 2·32 per cent. too much. In a separate set of determinations, with different solutions, the coefficient for the alkali, using methyl orange, was 1·0006 to 1·0008 in three experiments, whilst with phenolphthalein the value in five experiments was 0·9799 to 0·9804, or again more than 2 per cent. out, an error due to the colour change taking place when half of the carbon dioxide of the contained carbonate is disengaged, with the formation of bicarbonate.

For comparatively rough work, complete protection against the absorption of carbon dioxide is unnecessary when litmus or phenolphthalein are used as indicators; if methyl orange is used, such protection is not required, even for accurate work. With the latter indicator it might be thought that sodium hydroxide could advantageously be replaced by sodium carbonate, by dissolving 53·05 g. in a litre of water at 15° for an $N/1$ solution; this is not to be recommended, however, because a solution of sodium carbonate also gradually attacks glass, even when cold, taking up a small amount of alkali, and further, the solu-

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[1] *Indikatoren der Acidimetrie und Alkalimetrie*, p. 28.

[2] *Proc. 5th Congress Applied Chemistry*, 1903.

[3] *Z. angew. Chem.*, 1903, **16**, 820.

tion creeps up and evaporates at burette jets and on the neck of flasks, thus giving rise to serious errors, unless this action is continuously watched.

Potassium hydroxide solution is made up similarly to sodium hydroxide, allowance being made for its higher molecular weight and also for the greater proportion of impurities that are generally contained, in weighing out the quantity required for the preliminary solution.

Barium hydroxide solution is usually made of empirical strength. The following method is given by Stutzer.[1] Thirty-five g. barium hydroxide and 5 g. barium chloride are dissolved in 1 litre of water. To obtain a clear solution on filtration, the bottle for receiving the solution is washed out with very dilute hydrochloric acid, a layer of petroleum about 10 to 12 mm. deep placed on the bottom, and a funnel, with a long exit tube reaching down to the layer of petroleum, placed in the neck; a filter paper is carefully fitted into the funnel by moistening it with distilled water, and is then also partially filled with petroleum. The flask, containing the solution to be filtered, is placed at a higher level than the funnel and its contents syphoned off through the latter. The filtered solution is shaken by giving the contents of the bottle a rotatory motion, whereby contact with the air is reduced as much as possible.

In the following table the analytical value of $\frac{1}{1}$, $\frac{1}{2}$, $\frac{1}{5}$, and $\frac{1}{10}$ normal solutions of alkali are given, expressed in grams per c.c. of solution :—

	N/1	N/2	N/5	N/10
Hydrochloric Acid[1]	0·03646	0·01823	0·007292	0·003646
Nitric Acid[1].	0·06305	0·003152	0·01261	0·006305
Sulphuric Acid[1]	0·04904	0·02452	0·00981	0·004904
Phosphoric Acid[2]				
(*a*) With Methyl Orange .	0·07100	0·03550	0·01420	0·00710
(*b*) ,, Phenolphthalein .	0·03550	0·01775	0·00710	0·00355
Oxalic Acid[3]	0·06302	0·031501	0·012604	0·006302
Citric Acid[3]	0·07502	0·037501	0·015005	0·007502
Acetic Acid[3]	0·069802	0·034901	0·01396	0·006980
	0·06003	0·030015	0·012006	0·006003

[1] Towards all indicators.

[2] *Cf.* pp. 65 and 72; the values given are calculated for the anhydride P_2O_5.

[3] Towards litmus and phenolphthalein; the values given are calculated for the crystallised acids, including the water of crystallisation for oxalic and citric acids.

POTASSIUM PERMANGANATE

A solution of potassium permanganate is used for oxidising purposes, in which it gives up five-eighths of its oxygen, according to the equation :—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + O_5 + 3H_2O.$$

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[1] Private communication to Dr Böckmann.

Referring to the explanation given on p. 81, it will be seen that a normal solution would yield 0·008 g. available oxygen per c.c., and would be obtained by making up 31·64 g. pure potassium permanganate to a 1-litre solution. A solution of this strength would, however, be liable to crystallise at low temperatures, owing to the slight solubility of the salt; hence solutions stronger than $N/2$ are never prepared, and much more dilute solutions are very frequently used, *e.g.*, $N/10$, $N/20$, $N/50$, or even $N/100$. The use of such dilute solutions is, in this case, consistent with accuracy, since an indicator, in the ordinary sense of the term, is not used; on the other hand, when an indicator is specially added to show the end of a reaction, by means of a colour change, the latter is brought about by mass action between the ions, and hence the addition of a certain excess of the titration liquid is always necessary. In the case of permanganate solution, the very intense colour of the MnO'_4 ion is independent of the corresponding positive ion $H^\cdot$ or $K^\cdot$, etc. The liquid will, of course, remain colourless as long as the MnO'_4 ion is destroyed and converted into other colourless ions, according to the above reaction; at most, the solution will assume a slight coloration, owing to the formation of ions from other substances taking part in the reaction, *e.g.*, the formation of tervalent from bivalent iron. In the dilute solutions used for these titrations such colorations are extremely slight, and disappear altogether when compared with the colour of the permanganate ion. An excess of even one drop of $N/100$ permanganate solution in 100 c.c. or more water, produces the intense purple, or in small quantities, light-red colour of the permanganate ion, and thus indicates the end of the reaction.

The main reason for using the standard solution fairly strong is, that otherwise, in most cases, an inconveniently large volume of the solution would be required to complete the titration. Another reason why very dilute permanganate solutions should only be used in exceptional cases, is that permanganate acts on the impurities which are present even in ordinary distilled water, and its available oxygen is thus decreased. A freshly prepared permanganate solution should therefore never be used immediately, but should be left to stand for at least three or four, or better for eight to ten days, before it is standardised; the impurities in the water will then be completely oxidised. The standardisation of a very dilute permanganate solution cannot, however, be made very accurate by any method, since the weight of substance or volume of solution to be titrated must necessarily be small, and thus the unavoidable experimental errors greatly influence the result. The obvious artifice of first preparing a concentrated solution, standardising it accurately and then diluting, leads of course to inaccuracies, owing to the action of permanganate on the water used for dilution, and it is not easy to determine the extent of these errors and to allow for them. These difficulties can be surmounted by adding a little permanganate to the water to be used for dilution, and leaving it to stand for from eight to fourteen days; when it is only just possible to detect a pale red coloration on looking through a considerable depth of this water, it may be used for diluting stronger permanganate solutions without appreciable error. Again, no appreciable error is incurred if a permanganate solution is diluted with ordinary distilled water and used *immediately*, and this again leads to the conclusion that dilute permanganate solutions should not be kept in stock; strong solutions (at least 1/10 normal) should be prepared and accurately standarised and diluted to *N*/20, *N*/50, or *N*/100 for immediate use, according to requirements.

The permanganate solutions formerly used were unstable, because pure crystallised potassium permanganate was hardly obtainable, and the solutions contained manganate and deposited manganese dioxide. At the present time there is no reason why permanganate solution should not keep, provided it is protected from evaporation, dust, etc.

Oddy and Cohen[1] state that permanganate solutions lose 2 to 3 per cent. of their oxidising value in four months, whether exposed to light or not. Their observations, however, are insufficient in number and in accuracy. Treadwell[2] found that a well-protected permanganate solution lost only 0·17 per cent. of its oxidising value, after keeping for eight months; he recommends that the solution be re-standardised every two or three months, if great accuracy is required. Lunge has observed a decrease of 0·2 per cent. after three months, and agrees with Treadwell's recommendation.

For the sake of certainty, however, a check is desirable in this case, as with every standard solution which has been kept for lengthy periods; it is impossible to know to what extent small errors, due to some unknown source, may accumulate and finally produce an error which would vitiate results. If this condition is attended to, there is no reason why the value of the solution should be made empirical, necessitating the use of a factor every time a titration is to be calculated, as used formerly to be directed. On the contrary, solutions may be prepared in definite molecular proportions, just as in the case of standard acid or standard iodine solution; or, if estimations of only one particular kind are to be made, *e.g.*, iron estimations, the permanganate solution may be so prepared that 1 c.c. of the solution corresponds to (say) 0·010 g. iron.

Permanganate solutions are, of course, subject to change if in contact with organic matter; such change is made visible by a separation of brown manganese dioxide. Hence the solutions cannot be filtered through filter paper and must be protected from all forms of dust.

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[1] *J. Soc. Chem. Ind.*, 1890, 9, 17.

[2] *Analytical Chemistry*, vol. ii., p. 481.

They should be stored in bottles with well-fitting, ungreased glass stoppers. It is desirable to protect them from direct sunlight. Pinchcock burettes must not be used for permanganate titrations, on account of the rubber, although the error thus caused is, according to de Koninck,[1] much smaller than is usually assumed, and is in fact negligible in most cases. Gay-Lussac or other delivery burettes were formerly in use; burettes with glass stopcocks are now exclusively used, preferably without grease. Lunge[2] states that a small quantity of vaseline on the stopcock does not influence the results.

Permanganate solutions often deposit a small quantity of manganese dioxide on keeping; this should of course not be shaken up and mixed with the liquid, as such a procedure would obviously vitiate the results. On the other hand, the stock-bottle should be shaken before use, to mix the solution with the water which has evaporated and condensed on the interior of the empty part of the bottle; hence, as soon as such a deposit is noticed, the contents of the bottle should be left to settle for at least twenty-four hours and then carefully decanted into another bottle, neglecting the last portions containing the precipitate. The solution must then, of course, be re-standardised. For accurate work, it is better, however, only to use solutions which have not precipitated any manganese dioxide.

On account of the deep colour of concentrated solutions, the upper meniscus of the solution should be read; dilute solutions, on the other hand, allow of the lower level of the meniscus being read as usual. The floats (p. 48) designed for use with permanganate solution have disadvantages, and it is better to work with a reading screen (p. 49).

Permanganate titrations are generally carried out in sulphuric acid solution. Hydrochloric acid has the great disadvantage of acting on potassium permanganate, even in very dilute solution, chlorine being liberated; hence solutions containing chlorides cannot be titrated without special precautions. This point was investigated by Kessler, and subsequently by Zimmermann, who showed that perfect accuracy is attained, provided a fairly large quantity of manganous sulphate is added to the liquid to be titrated; a solution containing 200 g. of the crystallised salt per litre is used, and about 20 c.c. of this solution are added.[3] Even with this precaution available, the presence of chlorides should be avoided or limited as far as possible, since the marked colour of ferric chloride hinders the recognition of the end-reaction.

Pure, dilute nitric acid is, like sulphuric acid, indifferent to permanganate; the lower oxides of nitrogen, however, reduce permanganate, and this action affords the best method for their estimation.

[1] Private communication to Prof. Lunge.

[2] *Z. angew. Chem.*, 1904, **17**, 197.

[3] For an explanation of this action, *cf.* J. Wagner, *Massanalytische Studien*, p. 77; Gooch and Peters, *Z. anorg. Chem.*, 1899, **21**, 185; Skrabal, *Z. anal. Chem.*, 1903, **42**, 359.

A normal permanganate solution cannot be prepared by simply dissolving a weighed quantity of potassium permanganate and diluting to a definite volume, partly on account of the above-mentioned action on distilled water, and partly because the "chemically pure" commercial salt generally contains a little potassium sulphate, chloride, nitrate, or other impurities; it cannot be regarded as 100 per cent. potassium permanganate, although Gardner, North, and Taylor[1] have recently asserted the contrary. For these reasons, a little more than the calculated amount of the salt is weighed out, about 16 g. for $N/2$ solution, 3·2 g. for $N/10$ solution, etc.; this is made up to 1 litre of solution at 15°, and left to stand for about a week before standardisation. It is not advisable to dissolve the salt in the litre flask, as the presence of undissolved crystals may easily be overlooked, owing to the dark colour of the solution. The weighed quantity of the salt is preferably dissolved in warm water in a beaker, the solution poured into the litre flask, and any of the salt that may have remained behind in the beaker then dissolved in more water.

Very many methods have been suggested for fixing the strength of a permanganate solution; only a limited number of these can be referred to, and only a few will be described in detail.

The oxalic acid method was formerly regarded as the most reliable, provided the purity of the oxalic acid is ascertained by referring it back to pure sodium carbonate. Sörensen has, however, shown that sodium oxalate can be obtained quite pure and free from hygroscopic water, and his recommendation of this salt for the standardisation of permanganate solutions has been fully confirmed by Lunge (cf. *infra*).

1. Oxalic Acid method.—This method, proposed by Hempel, is based on the oxidation of oxalic acid, in presence of sulphuric acid, to carbon dioxide and water:—

$$5C_2H_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4.$$

The reaction proceeds slowly in the cold, rapidly at 40° to 50°; even at this temperature the first drops of permanganate are not immediately decolorised. When once the reaction has started, however, it proceeds rapidly, owing to catalytic action on the part of the manganese salt; the drops of permanganate are then decolorised the instant they reach the liquid, and the final colour change, from colourless to light red, is sudden and very sharp.

The above equation shows that $5 \times 90·03 = 450·15$ parts anhydrous oxalic acid require 80 parts oxygen; hence one part anhydrous oxalic acid corresponds to 0·17772 parts oxygen. This refers to anhydrous oxalic acid, whilst normal solutions of oxalic acid are prepared from the crystallised acid $C_2H_2O_4 . 2H_2O$, molecular weight 126·05, equivalent

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[1] *J. Soc. Chem. Ind.*, 1903, **22**, 731.

63·025. As Riegler[1] has pointed out, standard oxalic acid solutions may be rendered more permanent by an addition of sulphuric acid and by protecting them from light; nevertheless, these precautions by no means ensure absolute permanence of the solution, and this fact, quite apart from the absence of any guarantee of the purity and dryness of the oxalic acid, renders it impossible to apply the solution directly to the standardisation of permanganate.

If it be, nevertheless, desired to use this direct method, results of any practical value can only be obtained by using perfectly anhydrous oxalic acid, purified by the somewhat tedious method described above (p. 91), and not the pure commercial acid. The acid must be finally dried for six to eight hours at 60° to 80° in the weighing-bottle itself, and the bottle must be kept tightly closed during weighing; it is then dissolved in about 20 c.c. of water and strongly acidified with sulphuric acid.

But even when the method is thus modified, it is impossible to be certain that the results will be absolutely reliable. On the other hand, Lunge[2] has shown that accurate results are obtained by preparing a solution from pure, ash-free oxalic acid and determining its strength by acidimetry; thus the substance to which the permanganate is primarily referred is not a weighed quantity of oxalic acid, the amount of water in which can never be known with certainty, but sodium carbonate, which can be obtained in a condition of undoubted purity and dryness (*cf.* p. 83). In this method hydrochloric acid, best about $N/5$, is first standardised against sodium carbonate, using methyl orange as indicator, and this used to standardise a barium hydroxide solution of about $N/5$ strength (p. 92); the latter is then used to titrate the oxalic acid solution, with phenolphthalein as indicator, any excess of baryta being titrated back with $N/5$ hydrochloric acid. In this way the true amount of oxalic acid in the solution can be found, with a possible error of $\pm \frac{1}{2000}$, provided all necessary precautions are taken, viz., the use of calibrated burettes and pipettes, the introduction of corrections for temperature, etc. Fifty c.c. oxalic acid are then measured out, using the same pipette as was employed in the above acidimetric determination of the acid, 5 c.c. sulphuric acid and 200 c.c. water, at about 70° added, and the strength of the permanganate solution determined; 1 c.c. $N/5$ barium hydroxide solution corresponds to 0·012605 g. $C_2H_2O_4 . 2H_2O$, or 0·01118 g. Fe, or 0·0016 g. available oxygen.

The permanganate, thus standardised, should be used at once to determine the value of a stock of iron wire by method No. 2 described below. When it is subsequently required to standardise permanganate it is more convenient to titrate against this iron wire than against

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[1] *Z. anal. Chem.* 1896, **35**, 522; *J. Chem. Soc. Abstr.*, 1896, **70**, 676.

[2] *Z. angew. Chem.*, 1904, **17**, 268.

oxalic acid, since the permanence of the latter cannot be relied upon, nor can it be secured by addition of sulphuric acid, since this would exclude its standardisation by the above acidimetric method.

Kraut[1] has recommended the substitution of *potassium tetroxalate* (p. 92) for oxalic acid, as it can be prepared in a pure state and is permanent in the air. Ulbricht and Meissl, Meineke, and others recommend the use of this salt; as already stated, however (p. 92), its composition, whether dried at the ordinary or at a higher temperature, is far too uncertain. It should therefore only be employed when its value has been ascertained by the sodium carbonate, hydrochloric acid, barium hydroxide method.[2]

Rüst[3] gives the preference to *manganese oxalate*, prepared by precipitation and dried between filter paper; it is then said to exactly correspond to the formula with two molecules of water of crystallisation. This, however, would appear to be hardly reliable.

Barbieri and Neppi[4] employ ferrous oxalate.

Sörensen (*cf.* p. 85) recommends the use of chemically pure *sodium oxalate*, prepared by Kahlbaum from his directions; for accurate work the salt must be placed for a few hours in a drying oven at 100° and left to cool in a desiccator, over calcium chloride. It is then dissolved in water in a flask, and titrated in sulphuric acid solution. Ten c.c. $N/10$ potassium permanganate solution correspond to 67·05 mg. sodium oxalate, or 0·1 g. of the latter to 14·91 c.c. of the former. Lunge[5] confirms the accuracy of this method, and recommends it, in preference to all others, for the standardisation of permanganate.

2. Iron method.—Very fine soft iron wire is used as the basis of this method; it should be cleaned with emery paper and rubbed with writing paper before weighing. It is, of course, not pure iron and may contain 0·3 per cent. or more of impurity. As Treadwell has pointed out, this does not imply that the value of the wire is equal to that of the contained iron; on the contrary, it may exceed 100 per cent., owing to its content of carbon, silicon, phosphorus, etc. To avoid errors, which may be considerable, its value must be determined as described below.

To check an $N/2$ permanganate solution, a piece of wire weighing about 1·25 g., for an $N/10$ solution a piece weighing about 0·25 g., is weighed to within 0·0001 g. The wire is then stretched out, its length measured, and a number of pieces of the same length cut off; these can then be very rapidly weighed, as their approximate weight is known. Each piece will require nearly, but not more than, 50 c.c. of permanganate solution.

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[1] *Annalen*, 1863, **126**, 629.

[2] *Cf.* Reinhardt (communication to Meineke), *Z. öffentl. Chem.*, 1898, **4**, No. 13.

[3] *Z. anal. Chem.*, 1902, **41**, 606; *J. Soc. Chem. Ind.*, 1902, **21**, 1413.

[4] *Rend. Soc. Chim. Roma*, **3**, 16.

[5] *Z. angew. Chem.*, 1904, **17**, 230 and 269; 1905, **18**, 1520.

The weighed wire is then dissolved in hot dilute sulphuric acid, in absence of air; this may be effected in a flask fitted with a Bunsen valve (Fig. 38), or in any similar form of apparatus; or a flask provided with a tube, bent twice at right-angles and dipping into a beaker containing sodium bicarbonate solution, may be used. If the flame is removed when the iron has dissolved, the bicarbonate solution is sucked back and cools the contents of the flask, whilst the carbon dioxide evolved keeps out the air.[1] The device (Fig. 39), designed by Contat[2] and improved by Göckel,[3] is much more convenient than any of the above arrangements. It consists of a bulb provided with a syphon overflow tube, which is fitted into the flask in which the iron is dissolved. The amount of water or sodium bicarbonate solution, placed in the bulb at the beginning of the experiment, should be such that the end of the longer arm of the syphon just dips below its surface, and this level is not altered until boiling is finished; a saturated sodium bicarbonate solution is then poured into the bulb, which will be sucked into the flask as the contents cool, until the pressure of the carbon dioxide balances that of the air; the solution remaining in the bulb protects the contents of the flask from the air.

Fig. 38.

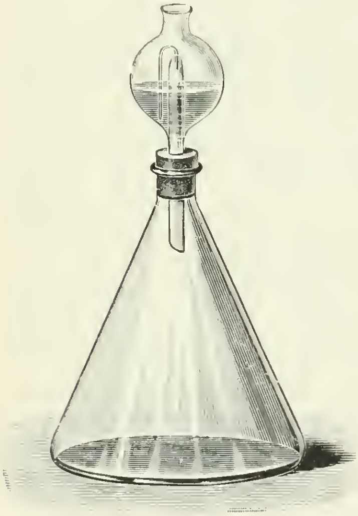

Fig. 39.

The standardisation of permanganate by means of iron has been subjected to detailed investigation by Skrabal.[4] He found that the apparent value of a sample of iron wire, when determined by permanganate, was 100·03 to 100·21 per cent., whereas the actual amount of iron contained was only 99·38 per cent. (together with 0·03 P, 0·31 Mn, 0·185 Cu, 0·023 S, 0·09 C). He therefore rejects the method as unreliable, and attributes its inaccuracy to the fact that although the carbide in the wire is not decomposed, even by boiling with permanganate, it is decomposed when warmed with permanganate for a long time in presence of a ferrous salt, since it acts as an "acceptor" in the oxidisation of the ferrous sulphate. For the standardisa-

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[1] Jahoda, *Z. angew. Chem.*, 1889, **12**, 87.

[2] *Chem. Zeit.*, 1898, **22**, 298.

[3] *Z. angew. Chem.*, 1899, **12**, 620; *J. Soc. Chem. Ind.*, 1899, **18**, 708. The apparatus is made by Alt, Eberhard, & Jaegar, Ilmenau, and by Göckel & Sauer, Berlin.

[4] *Z. anal. Chem.*, 1903, **42**, 359.

tion Skrabal uses either chemically pure iron, or iron wire of known composition, *i.e.*, of definite value; the iron is dissolved in sulphuric acid, 15 c.c. $N/10$ permanganate added to the warm solution, which is then left to stand over-night in a warm place, whereby the carbides are completely oxidised; concentrated hydrochloric acid is then added, the solution heated to boiling, reduced with zinc, and titrated with permanganate. These directions are doubtless good, but uniform and correct results can be obtained without this complication, provided due care is taken to adhere to the same conditions of dilution, heating, etc., both in standardising and in the subsequent use of permanganate.

The cold iron solution is titrated with permanganate until a faint rose-red coloration is obtained, and remains permanent for thirty seconds; it is not necessary that it should be permanent for longer. If the number of c.c. used is divided into the number which would have been required had the permanganate been accurately normal, a coefficient is obtained by which every reading must be multiplied; it is preferable, however, to dilute the solution to the normal value. Supposing 40·00 c.c. of a correct normal solution would have been required, whilst in the experiment only 39·00 c.c. were used, then the coefficient is $\frac{40{\cdot}00}{39{\cdot}00} = 1{\cdot}0256$; hence the solution will be corrected by the addition of 25·6 c.c. of water to every 1000 c.c. of the solution.

In order to avoid the uncertainty due to the composition of the iron wire, Classen has proposed the use of electrolytically deposited iron. The iron is deposited on a platinum dish, by electrolysing a solution of ferrous ammonium sulphate containing ammonium oxalate; the deposited iron is washed with water and alcohol, dried at 80° to 100°, weighed, dissolved in sulphuric acid, and the solution titrated with permanganate whilst still in the dish. Even supposing that the electrolytically deposited iron is pure, it is questionable whether oxidation during drying and dissolving is not a source of greater errors than are incurred when iron wire is dissolved in a flask provided with a valve, assuming the actual percentage of iron to be 99·8.

Treadwell[1] also recommends the electrolytic method, which he modifies by depositing the iron on a small cylinder of platinum foil and dissolving it in air-free sulphuric acid, in a current of carbon dioxide.

Skrabal[2] found 0·10 to 1·47 per cent. impurities, including hydrogen, in electrolytic iron obtained by Classen's method. He gives an alternative method for preparing pure electrolytic iron, but according to Classen,[3] the iron thus obtained is not pure.

Avery and Dales[4] have shown that iron, deposited electrolytically from ammonium oxalate solutions, contains 0·21 to 0·42 per cent. of

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[1] *Analytical Chemistry*, vol. ii., p. 81.

[2] *Z. anal. Chem.*, 1903, **42**, 359.

[3] *Ibid.*, 1903, **42**, 516.

[4] *Berichte*, 1899, **32**, 64 and 2233.

carbon, and that a small quantity of iron, on an average 0·35 per cent., is always left in solution. Whilst Verwer and Groll[1] contend that the deposition is complete and free from carbon, the results of Avery and Dales have been fully confirmed by Kohn, Brislee, and Froysell.[2] According to their experiments, the electrolytic method gives results from 0·2 to 0·3 per cent. too high, calculated on the weight of iron deposited, and its apparent accuracy is due to the compensating errors of incomplete deposition and the presence of carbon; the percentage of the latter varies from 0·43 to 0·74, according to the length of time of the electrolysis, whilst 0·1 to 0·2 per cent. of iron is left in solution.

Ledebur[3] states that he has never found the value of iron wire to exceed 100 per cent., and that it is safe to use the percentage of pure iron present, as a basis; to determine this percentage, however, accurately to within 0·1 per cent. is a matter of great difficulty, and in any case carbides, etc., notoriously act as reducing agents.

According to Lunge,[4] electrolytic iron cannot be relied upon as pure; on the contrary, its use may lead to errors of several units in the first place of decimals. It is very much better to determine the value of a large stock of iron wire by means of permanganate, after having previously standardised the latter by oxalic acid, referred to pure sodium carbonate (p. 104). Since sodium oxalate is free from all the uncertainties connected with the use of iron, it forms a far more reliable basis for standardisation than the latter.

3. **Ferrous Ammonium Sulphate method.** — The double salt $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$, sometimes called Mohr's salt, is more stable than ferrous sulphate, and was therefore recommended by Mohr for standardising permanganate. The dissolving of the iron is avoided and the errors arising from the uncertainty, due to the variable amount of carbon in iron wire are eliminated. Still greater uncertainty is, however, introduced, owing to the presence of water of crystallisation and of impurities in the salt. The commercial salt is quite unreliable, and it is difficult to prepare a perfectly pure salt containing exactly the right amount of water of crystallisation. Where errors of some tenths per cent. are not of consequence, this salt may be used for standardising; it cannot be recommended for accurate work. The value of the salt is 14·29 per cent. of that of iron, *i.e.* almost exactly one-seventh.

Graeger, and subsequently Biltz, proposed the use of ferrous sodium sulphate, $Na_2SO_4 . FeSO_4 . 4H_2O$, in place of the ammonium salt, but it has not come into general use.

Meineke[5] also considers ferrous ammonium sulphate to be quite unreliable, and recommends the use of iron alum; this is reduced with

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[1] *Berichte*, 1899, **32**, 806.

[2] *British Association Reports*, 1900, p. 174.

[3] *Stahl und Eisen*, 1902, **22**, 1242; *cf.* also, Thiele and Deckert, *Z. angew. Chem.*, 1901, **14**, 1233.

[4] *Z. angew. Chem.*, 1904, **17**, 265.

[5] *Z. öffentl. Chem.*, 1898, **4**, No. 13.

stannous chloride, mercuric chloride finally added, and the solution then titrated with permanganate, following Reinhardt's directions.[1] The amount of iron in the "chemically pure" iron alum must be checked by precipitation with ammonia. Wdowiszewski[2] has proposed a method in which he prepares "chemically pure ferric oxide"; this is reduced with stannous chloride, and then used to standardise permanganate. Gintl[3] uses a spiral of palladium wire, saturated with hydrogen, as reducing agent, and prefers this to all other methods of reduction.

4. **Volhard's[4] Iodimetric method.**—If a permanganate solution is added to a solution of potassium iodide, acidified with hydrochloric or sulphuric acid, a quantity of iodine is liberated, which is equivalent to the amount of available oxygen in the permanganate. The iodine dissolves in the excess of potassium iodide solution, and its amount can be determined by adding excess of sodium thiosulphate and titrating back with standard iodine solution:—

$$KMnO_4 + 5KI + 8HCl = 5I + 6KCl + MnCl_2 + 4H_2O.$$

This process, though theoretically quite correct, has the disadvantage of requiring two additional standard solutions, on the accuracy of which the process is dependent; the unavoidable summation of small errors may easily lead to a final error of several tenths per cent.

Volhard gives a series of examples, according to which his method gives similar results to those obtained with sodium oxalate, iron ammonium alum and iron wire. The data, however, show discrepancies up to 0·3 per cent., and it must be borne in mind that both iron ammonium alum, and iron wire may lead to errors of several units in the first place of decimals, when used for the primary standardisation of permanganate, so that Volhard's examples cannot be considered as proof of the accuracy of his method. F. Dupré[5] states that the method gives accurate results.

5. **Titration with Hydrogen Peroxide.**—Morse and Chambers[6] add neutral hydrogen peroxide to a measured volume of standard sulphuric acid; permanganate solution is then run in from a burette, until only a small excess of hydrogen peroxide remains, and the free acid is then titrated back. The decomposition is represented by the equation:—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

6. **Gas-volumetric, Hydrogen Peroxide, or Nitrometer method.**[7]—This method is not used as frequently as it deserves, partly because all laboratories are not provided with the necessary apparatus, although it

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[1] *Stahl und Eisen*, 1884, 4, 704; *Chem. Zeit.*, 1889, 13, 323.

[2] *Stahl u. Eisen*, 1901, 21, 816.

[3] *Z. angew. Chem.*, 1902, 15, 431.

[4] *Annalen*, 1879, 198 333.

[5] *Z. angew. Chem.*, 1904, 17, 815.

[6] *Amer. Chem. J.*, 1896, 18, 236; *Z. anal. Chem.*, 1898, 37, 183.

[7] Lunge, *J. Soc. Chem. Ind.*, 1890, 9, 21. *Cf.* also, H. v. Jüptner, *Osterr. Zeit. für Berg. und Hüttenwesen*, 44, 371; Vannino, *Z. angew. Chem.*, 1890, 3, 80; *J. Soc. Chem. Ind.*, 1890, 9, 552.

is applicable to a number of other purposes, and partly because it belongs to a sphere foreign to the usual applications of permanganate. It has certain fundamental advantages over all other methods. It requires neither balance nor weights, a point of interest rather than of practical importance; more important is the fact that it dispenses with the use of any primary substance of undoubted purity, the requirement which puts such great difficulties in the way of other methods. In addition, none of those detours are involved which lead to an accumulation of small errors. The available oxygen is measured directly, with the qualification that its volume is doubled by an equal volume of oxygen derived from the hydrogen peroxide, which halves the error of measurement. The gas is measured over mercury, so that the measurement can quite easily be made accurate to 1/40 c.c., and an accuracy to 1/100 c.c. can be attained by taking special precautions, such as reading the volume of gas with a cathetometer, etc.; since the volume of gas measured exceeds 100 c.c., the error in measurement is reduced to 1/4000 or 1/10000, provided an accurately calibrated nitrometer is used, a degree of accuracy which cannot be attained with burettes, etc. The use of an accurate thermometer and barometer, or as an alternative, of a calibrated "gas-volumeter" and an accurately adjusted "reduction tube," are, of course, assumed. This degree of accuracy will not be attained in the standardisation of dilute permanganate solutions, since the amount of liquid which can be treated in the nitrometer is limited; but this applies to all other methods, since the standardisation of dilute solutions is always relatively less accurate than that of strong solutions (p. 100).

The method is based on the following reaction between hydrogen peroxide and a solution of potassium permanganate, strongly acidified with sulphuric acid:—

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Thus, whichever of the reagents is not in excess gives up the whole of its available oxygen, and this is increased by an exactly equal volume of oxygen derived from the other reagent.

The available oxygen in hydrogen peroxide can be determined by decomposing it with an arbitrary amount of permanganate, provided the latter is in excess, and similarly the available oxygen in permanganate can be estimated by using an excess of hydrogen peroxide; it is then only necessary to measure the volume of oxygen evolved, to reduce this volume to 0° and 760 mm., and halve the result. The reaction proceeds quite smoothly and is quantitative; the solutions retain no oxygen, since they were previously saturated with air. Certain simple precautions must be observed: viz., a large excess of sulphuric acid must be present, but not too large an excess of hydrogen peroxide; the apparatus must be adjusted immediately the solutions have been mixed, and attention must be paid to those conditions which must be observed in all gasometric methods, such as uniformity of temperature, etc. The latter is easily attained, since the reaction involves no appreciable rise of temperature.

Any form of apparatus for gasometric analysis can be used for the determination; to ensure great accuracy, the evolved gas should be measured over mercury. Lunge's nitrometer with attached bottle is particularly suitable for the decomposition, and by employing it or similar apparatus, in conjunction with a "gas-volumeter," the calculation of the volume of oxygen to standard conditions is saved. Both instruments will be described subsequently (pp. 132 and 138); the following description is therefore restricted to their application to the valuation of permanganate solutions.

Since 1 litre of dry oxygen at 0° and 760 mm. weighs 1·429 g. in these latitudes, and half of the evolved oxygen comes from the permanganate, every c.c. of the measured volume corresponds to 0·7145 mg. available oxygen in the permanganate. Hence 1 c.c. of an accurately semi-normal permanganate solution will give 5·597 c.c. of oxygen (N.T.P.); an $N/10$ solution will give 1·119 c.c. oxygen per c.c. of solution, and so on. It is not practicable to decompose much more than 20 c.c. of permanganate solution at a time, so that it is best to take exactly 20 c.c. An $N/2$ solution will then give about 112 c.c. gas (N.T.P.), an $N/10$ solution about 20 c.c.; ordinary conditions of temperature and pressure will increase these volumes by from 5 to 15 per cent., so that for an $N/2$ solution a nitrometer with a 150 c.c. bulb tube should be used; for an $N/10$ solution, one with a 50 c.c. straight tube will suffice.

The valuation is conducted as follows: 20 c.c. of permanganate solution are accurately measured into the outer compartment of the decomposition bottle and 30 c.c. dilute sulphuric acid (1 : 5) added. For $N/2$ permanganate, 15 c.c. ordinary commercial hydrogen peroxide are then introduced into the inner vessel of the decomposition bottle, by means of a pipette; for weaker solutions less peroxide is taken. A preliminary experiment should be made, in a beaker, to ensure the presence of an excess of hydrogen peroxide; any considerable excess is unnecessary and may constitute a source of error, but the results are quite accurate even when double the theoretical amount of hydrogen peroxide is taken. The decomposition bottle is then closed by the stopper, and the resulting excess pressure relieved by momentarily opening the tap of the measuring tube; after making sure that the mercury fills this tube right up to the tap, the latter is turned so that the measuring tube communicates with the decomposition bottle. The solutions in the bottle are then mixed, by tilting, and the bottle shaken for exactly three minutes; shorter shaking is not sufficient, and longer shaking may vitiate the results. The level of the mercury in the pressure tube and the measuring tube is then adjusted and the stopcock closed. The decomposition bottle should be held by the rim when being shaken, and the usual precautions must be taken to avoid any warming of the measuring tube and bottle. For accurate work, it is preferable to place the bottle, before the decomposition, in a vessel containing water at the temperature of the room, and to replace it in this vessel after shaking and before adjusting the pressure tube, so that the temperature is the same at the beginning and at the end of the experiment.

The volume of gas in the measuring tube is then calculated to N.T.P., allowance of course being made for the tension of aqueous vapour; or the correction may be made by the gas volumeter. Each c.c. of the corrected volume equals 0·7145 mg. available oxygen in the permanganate used; supposing that 20 c.c. of the latter gave 112·75 c.c. gas, then 1 c.c. permanganate would contain $\frac{112{\cdot}75 \times 0{\cdot}7145}{20} = 4{\cdot}031$ mg. available oxygen. This corresponds to a solution a little stronger than semi-normal, and having the factor 1·0077.

The oxalic acid and iron methods require an appreciably longer time to carry out than this hydrogen peroxide method, and are, moreover, dependent upon the use of pure substances. The deviations in these methods do not exceed 1/1000, which is really the limit of possible accuracy in individual observations with them all; this has been shown both by Lengfeld[1] and by Lunge.[2] Comparative experiments by Vanino,[3] using the azotometer and the iodimetric method, confirm this conclusion; this author gives a table for the weight of 1 c.c. of oxygen at different temperatures and pressures.

The applications of permanganate are extremely numerous, and include the estimation of iron, oxalic acid and oxalates, nitrous acid and nitrites in sulphuric acid solution, potassium ferrocyanide, tanning materials, and hydrogen peroxide; it is also used indirectly, for titrating back excess of reducing agents, *e.g.*, ferrous oxide in the estimation of nitric acid, nitrates, chlorates, manganese dioxide, peroxides, bleach, etc.

IODIMETRY

The iodimetric methods of volumetric analysis were introduced by Bunsen, and are now very extensively used; they are amongst the most accurate known, owing to the extreme sensitiveness of the indicator, starch solution, that is employed.

Iodine oxidises many substances indirectly, by combining with the

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[1] *Z. angew. Chem.*, 1890, **3**, 11.

[2] *Ibid.*, 1904, **17**, 270.

[3] *Ibid.*, 1890, **3**, 80; *J. Soc. Chem. Ind.*, 1890, **9**, 552.

hydrogen of water, liberating the oxygen, which then combines with other compounds present. In other cases it combines directly with the hydrogen or sodium in the substance to be estimated, as in the determination of hydrogen sulphide and of sodium thiosulphate.

The "re-sublimed iodine" of commerce is a very pure product, which may be used for many purposes without further purification; it only requires to be dried in the exsiccator to free it from water, for the preparation of normal solutions. For accurate standardisation, however, the iodine must be further purified (p. 118).

An $N/10$ iodine solution is generally used; it is prepared as follows: 12·7 g., or a little more, pure re-sublimed iodine are weighed out on a rough balance and shaken into a litre flask containing a solution of 15 to 18 g. potassium iodide in about 30 g. water; the flask is closed, shaken till the iodine is completely dissolved, and then filled up to the mark. The solution is then titrated against $N/10$ arsenious oxide or sodium thiosulphate solution, previously standardised by perfectly pure iodine (p. 118).

For the estimation of small quantities of sodium sulphide a special solution, prepared by dissolving 3·252 g. pure iodine and 5 g. potassium iodide and diluting to 1 litre, is sometimes used; 1 c.c. of this solution =0·001 g. sodium sulphide.

The use of $N/100$ iodine solutions has been recommended, on the ground that it can be used in pinch-cock burettes; experiments by Lunge[1] have shown, however, that such dilute solutions readily attack rubber. Further, a comparatively large excess is necessary to give a distinct blue coloration with starch, though this disadvantage can be lessened by using a large excess of potassium iodide.[2] Iodine solutions should be kept in well-stoppered bottles and stored in a cool place; the strength should be checked about once a month, as the contained iodine is distinctly volatile. For this reason the solution, when in use, should be kept out of contact with the air as much as possible, and the titrations should be conducted in bottles or narrow-necked flasks, not in beakers or dishes; for the same reason, the iodine should be run into the solution to be titrated, whenever possible, and not *vice versa*. This does not apply to the titration of sulphites, since the action of atmospheric oxygen on the sulphite must be avoided (cf. *infra*). Burettes with glass taps should be used and the taps greased with vaseline. The top of the burette should be kept well closed, and only be opened sufficiently, when in use, to allow the solution to flow from the burette. The volatility of iodine must also be borne in mind when gases containing sulphur dioxide or sulphuretted hydrogen are bubbled through iodine solution, in order to absorb these gases.

In conjunction with the iodine solution, starch solution is used as

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[1] *Z. angew. Chem.*, 1904, 17, 197.

[2] Treadwell, *Analytical Chemistry*, vol. ii., p. 513.

the indicator, and either sodium thiosulphate or arsenious oxide solutions, of corresponding strength, as the reducing solution.

Starch solution may be prepared as follows:—3 g. potato starch are ground with a little water to a uniform paste, and gradually added to 300 g. boiling water in a porcelain dish; boiling is continued until an almost clear solution is obtained. This is allowed to settle in a deep vessel, and the clear liquid filtered and saturated with common salt. The solution keeps for a considerable time if kept in a cool place; it should be discarded as soon as fungoid growths are observed in it. The addition of mercuric iodide[1] preserves the solution.

Zulkowsky's soluble starch is a more convenient reagent; it is obtained in the form of a thick paste, which should not be allowed to dry up; a small quantity is taken out, on the end of a glass rod, as required for use.

De Koninck[2] recommends grinding 2 g. of potato starch into a paste with cold water and adding this to a litre of boiling water; the whole is then boiled for two or three minutes, and 8 c.c. of a 10 per cent. solution of potassium iodide, saturated with mercuric iodide, added. The solution is allowed to cool, poured into a tall glass cylinder, and the clear portion decanted, after standing for one or two days. Starch solutions prepared in this way keep perfectly well for years.

Wroblewski[3] uses potassium hydroxide for preparing soluble starch, Förster,[4] hydrochloric acid, and Syniewski,[5] sodium peroxide. Another preparation is known as "ozone starch" (manufactured by C. Conrad, Kyritz); this is best rubbed up with cold water, poured, with stirring, into boiling water and rapidly cooled. The solution keeps for a considerable time, but mould develops after three or four weeks.

Iodine solution is generally standardised by an accurate solution of sodium thiosulphate or of arsenious oxide, the strength of which has been fixed by pure iodine (p. 118). It may also be directly standardised by a gasometric method, using the nitrometer; in this case the following directions must be accurately adhered to. Fifty c.c. of the iodine solution are placed in the outer compartment of the decomposition bottle, and a freshly prepared, *cold* mixture of 6 c.c. of 2 per cent. hydrogen peroxide and 8 c.c. of 50 per cent. potassium hydroxide are placed in the inner vessel. Any considerable excess of hydrogen peroxide must be avoided, and its strength must not exceed 2 per cent. After connecting with the measuring tube, a circular motion is first communicated to the bottle without allowing the solutions to mix; the bottle is then suddenly tilted through 90°, so as to effect an instantaneous and intimate mixing of the two solutions. After shaking for not more than a few seconds

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[1] Mutniansky, *Z. anal. Chem.*, 1897, **36**, 220.

[2] Private communication to Prof. Lunge.

[3] *Chem. Zeit.*, 1898, **22**, 375.

[4] *Ibid.*, 1897, **21**, 41.

[5] *Ber.*, 1897, **30**, 2415; 1898, **31**, 1791.

the pressure is adjusted and the volume of gas read off. One c.c. oxygen corresponds to 0·011331 g. iodine according to the equation :—

$$I_2 + H_2O_2 = 2HI + O_2.$$

Kalmann[1] recommends sodium sulphite for the standardisation of iodine. A solution of arbitrary strength is run into the iodine solution until it is just decolorised, when the following reaction takes place :—

$$Na_2SO_3 + 2I + H_2O = 2HI + Na_2SO_4.$$

Thus the acid liberated is exactly equivalent to the iodine. The acid is then estimated by standard potassium hydroxide, using methyl orange as indicator. The method is independent of the amount of water and of sulphate in the sodium sulphite, provided the latter is perfectly free from bisulphite, thiosulphate, and carbonate. The decomposition goes best when the solution is not too dilute. One c.c. $N/10$ alkali hydroxide corresponds to 0·012697 g. iodine.

The principle of this method is perfectly sound, but the difficulty of obtaining sulphite free from bisulphite, thiosulphate, or carbonate makes it practically useless for standardisations; "chemically pure" sodium sulphite generally contains some carbonate. A way out of this difficulty would be, to add phenolphthalein and $N/5$ hydrochloric acid till decolorised, to decompose the carbonate present, forming sodium bicarbonate, then a further quantity of hydrochloric acid equal to that already used, thus converting the bicarbonate into sodium chloride and obtaining a perfectly neutral solution of sodium sulphite; but this method is not practicable at ordinary temperatures, experiments by Lunge[2] having shown that under these conditions the colour change is gradual and uncertain.

S. W. Young[3] recommends anhydrous sodium thiosulphate for standardising iodine solutions; tartar emetic has been proposed by Metzl,[4] and potassium bichromate by Bruhns[5] and others.

Kalmann's method can, of course, be conversely applied to the determination of sulphurous acid, but it offers no advantage over direct titration with iodine, and is, in fact, less accurate; further, it may be used for determining sulphite, in presence of thiosulphate, by running the latter from a burette into a measured volume of standard iodine until just decolorised, and then titrating with $N/10$ sodium hydroxide and methyl orange. The sulphite is given by the amount of iodine equivalent to the alkali used; by subtracting this amount from the total iodine used, the iodine corresponding to the thiosulphate is obtained.

Experiments by Finkener, Volhard, and others have shown that the reaction between iodine and sulphurous acid or sodium sulphite is only quantitative, provided the solution of the latter is added drop by drop,

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[1] *Ber.*, 1887, **20**, 568.

[2] *Z. angew. Chem.*, 1904, **17**, 235.

[3] *J. Amer. Chem. Soc.*, 1904, **6**, 1028.

[4] *Z. anorg. Chem.*, 1906, **48**, 156.

[5] *Ibid.*, 1906, **49**, 277.

with stirring, to the iodine solution; in the reverse process too little iodine is used. This has been confirmed by Raschig.[1]

Berg[2] has pointed out that this is not due to the formation of hydrosulphurous acid, as Volhard supposed, but rather to the action of atmospheric oxygen on sulphur dioxide and to volatilisation of the latter; by following the above directions this effect is more easily avoided than when the iodine is added to the sulphurous acid solution.

Rupp[3] states that sulphur dioxide can be accurately titrated in alkaline solution containing bicarbonate. This can only be done, however, by adding an excess of iodine, leaving it to react for fifteen minutes and then titrating back, as the oxidation velocity of sulphites is appreciably smaller than that of free sulphurous acid. According to Ruff and Jeroch,[4] the correct results obtained by this method are due to a fortuitous compensation of errors. Accurate results can be obtained by omitting the back-titration, and by excluding the action of oxygen, by the addition of mannitol and working in an atmosphere of carbon dioxide.

The applications of iodine solution, known as iodimetry, generally in conjunction with a corresponding sodium thiosulphate or arsenious acid solution, are very numerous, and include the following estimations:—

Sulphurous acid, either as gas, or in very dilute aqueous solution, or dissolved in water, to any concentration, in the form of salts; if free sulphurous acid has to be estimated, it need only be neutralised by sodium carbonate. The sulphite solution must be added to the iodine, not *vice versa* (p. 115).

Thiosulphates are converted into tetrathionates (cf. *infra*).

Free *Chlorine* and *Bromine* are estimated by liberating iodine from potassium iodide. Similarly, the chlorine of hypochlorous acid and of hypochlorites may be determined; Lunge has proposed the following method for their simultaneous estimation. When potassium iodide acts on hypochlorous acid, half as much alkali is liberated as when it acts on hypochlorites:—

$$HOCl + 2KI = KOH + KCl + I_2$$
$$NaOCl + 2KI + H_2O = 2KOH + NaCl + I_2.$$

Hence free hypochlorous acid liberates two equivalents of iodine to one equivalent of potassium hydroxide, and any excess of alkali above this is a measure of the amount of hypochlorite present.

Bleach may be estimated by iodimetry, but it is better to titrate it directly with arsenious acid solution (p. 122).

Sulphuretted hydrogen and *Sulphides* react as follows:—

$$H_2S + I_2 = 2HI + S.$$

This decomposition is quantitative when the solutions are dilute, and are

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[1] *Z. angew. Chem.*, 1904, **17**, 579.

[2] *Bull. Soc. Chim.*, 1902 [3], **27**, 1077; *Chem. Centr.*, 1903, **1**, 249.

[3] *Ber.*, 1902, **35**, 3694.

[4] *Ibid.*, 1905, **38**, 409.

protected from the oxygen of the air. Hence also, all those substances may be thus estimated which liberate sulphuretted hydrogen on decomposition with hydrochloric acid, the evolved gas being absorbed in iodine solution.

Arsenious oxide:—

$$As_2O_3 + 2H_2O + 4I = As_2O_5 + 4HI.$$

Manganese dioxide and *other Peroxides*.

Chloric acid, *Chromic acid*, and their salts may be decomposed by hydrochloric acid, the chlorine liberated absorbed in potassium iodide, and the resulting free iodine estimated. Many methods may be included under this head, in which chromate is added in excess and the excess titrated back.

Iodimetry may also be made use of in connection with *Acidimetry*; the following reaction ensues on acidifying a mixture of potassium iodate and excess of potassium iodide:—

$$KIO_3 + 5KI + 6HCl = 6I + 6KCl + 3H_2O.$$

The free iodine is estimated by thiosulphate or arsenite solution, and thus the accuracy of iodimetry may be conveyed to acidimetry. This reaction may also be made the basis for the estimation of *free alkali*, by adding an excess of standard acid to the solution and then estimating the excess of the latter, as above.[1]

Many ascribe a much greater accuracy to iodimetry than to alkalimetry, and this is correct in so far that the iodine-starch reaction is much more sensitive and obvious than are the colour changes of alkalimetric indicators. But when the volatility of iodine and the recognised uncertainties in calibrating apparatus and in taking readings are taken into account, an accuracy of $\pm \frac{1}{1000}$ of the total may be considered as good work; this degree of accuracy can also be attained or even exceeded with litmus or methyl orange in acidimetry, provided every care is taken.

SODIUM THIOSULPHATE

An $N/10$ solution is prepared by dissolving 24·83 g. of the pure crystallised salt $Na_2S_2O_3 . 5H_2O$ in water, which has been completely freed from air by boiling; the solution is diluted to 1 litre with cold air-free water.

Meineke[2] states that pure sodium thiosulphate can be obtained by repeatedly recrystallising the "chemically pure" commercial salt from water and then rubbing it to a fine powder with strong alcohol. The resulting magma is thoroughly washed on the filter pump with pure ether, and dried on the pump until the ether is almost completely evaporated; the powder is then removed from the filter, covered over with paper, left to dry in the air for twenty-four hours, and then trans-

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[1] Gröger, *Z. angew. Chem.*, 1890, **3**, 353 and 385.

[2] *Chem. Zeit.*, 1894, **18**, 33.

ferred to a tightly closed bottle. According to Meineke, the salt prepared by this method is pure enough (99·99 per cent.) to be used for standardising iodine solution, but this is not the case, because the percentage of water in the salt is by no means reliable.

Pure sodium thiosulphate should dissolve in water without the least turbidity, should give no precipitate with barium chloride (a precipitate would indicate the presence of sulphate, sulphite, or carbonate), and should not redden phenolphthalein, (presence of carbonate). It should also be free from sulphide and chloride.

Iodine and sodium thiosulphate react with the formation of sodium tetrathionate, the iodine combining with half the sodium :—

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$

Whenever possible, the iodine is added to the thiosulphate solution; the latter should be neutral or faintly acid, because if more strongly acid free thiosulphuric acid is formed, which decomposes on standing into water, sulphur dioxide, and free sulphur. A slight yellow coloration is observed as soon as an excess of iodine is present. The change is sharper in presence of starch solution, but the blue coloration is only obtained at ordinary temperatures. Starch solution must never be added whilst a large excess of iodine is present; for instance, if the thiosulphate or arsenic solution is run into the iodine the starch is decomposed by the iodine, forming variously coloured compounds. The starch should be added towards the end of the reaction, when only very little iodine is present, if the titration is done in this way.

When the iodine solution has been accurately standardised, the thiosulphate solution may be prepared from the ordinary "pure" commercial salt; it is then compared with the iodine, and corrected.

The following method may be used as a further check on the thiosulphate solution and serves as a means for its standardisation, and indirectly for that of iodine solution. A small quantity of pure, dry iodine is prepared, by powdering together 0·5 g. pure iodine and 0·1 g. potassium iodide and heating the powder in a small porcelain dish on a sand-bath, or on an asbestos card, until vapour is copiously evolved; the dish is then covered with a dry watch-glass, and the greater part, but not the whole of the iodine, is sublimed on to the latter. The watch-glass is then covered with a second, accurately fitting glass and the whole weighed, the weight of the two watch-glasses of course being known. The watch-glasses are placed gently in a solution of 1 g. potassium iodide in 10 g. water; after waiting for a moment, to allow the iodine to dissolve, the solution is diluted with 100 c.c. of water and titrated with the thiosulphate solution. The potassium iodide must be free from potassium iodate; a test for its purity in this respect consists in adding hydrochloric acid to a not too concentrated solution of the salt, when no immediate yellow coloration develops, in absence of iodate. When the colour has been reduced to a pale yellow, a little starch solution is added and the titration continued until the blue colour just disappears. If the thiosulphate solution is of right strength, the amount used in c.c. multiplied by 0·012697 equals the weight of iodine taken.

According to Lunge, this method of preparing, weighing, and dissolving pure iodine is perfectly accurate in the hands of a fairly experienced worker, and when due attention is paid to the obvious necessity of rapid work, to guard against the volatilisation of the iodine. The following modification of the method recommended by Treadwell[1] is easier to carry out. Two to 2·5 g. pure potassium iodide and not more than 0·5 c.c. water are placed in each of two or three small weighing tubes with tightly fitting, ground stoppers; the tubes are closed and weighed, and then 0·4 to 0·5 g. pure iodine added to each, and weighed again. The iodine dissolves almost instantly in the concentrated potassium iodide solution. One of the tubes is then placed in the neck of a 500 c.c. Erlenmeyer flask, held in an inclined position and containing 200 c.c. of water and about 1 g. potassium iodide. The tube is dropped carefully to the bottom of the flask, the stopper being removed just as it begins to fall, and allowed to follow it. In this way no iodine can be lost. The examples given by Treadwell show deviations of about 0·2 per cent. from each other; these deviations can be reduced to 0·1 per cent., when using the first method given above, after considerable practice.

Winkler has proposed a method for preparing pure iodine in quantity, which consists in adding 5 per cent. potassium iodide and 10 per cent. quicklime (to retain water) to the crude iodine; the mixture is sublimed from a vessel covered with a flask filled with water, on which the sublimed iodine condenses. A funnel, the tube of which is loosely plugged, serves equally well to collect the iodine.

De Koninck's[2] method of preparing pure iodine for standardisation is as follows:—Potassium iodide is freed from potassium cyanide by recrystallising in presence of a little hydriodic acid; one part of the recrystallised salt is then intimately mixed with 1¾ parts previously fused potassium bichromate, both having been finely powdered and dried, and the mixture placed in a small retort, the neck of which fits tightly into a small Erlenmeyer flask. The latter is previously weighed along with a blown glass bulb, which subsequently serves as a stopper; the weight of the condensed iodine can thus be determined. The retort is gradually heated to incipient redness, the neck being sufficiently warmed to prevent iodine condensing in it; the flask must

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[1] *Analytical Chemistry*, vol. ii., p. 507.

[2] *Chem. Zeit.*, 1903, **27**, 192.

be protected from the heat by an asbestos card. The yield of iodine exceeds 95 per cent. The reaction is :—

$$6KI + 5K_2Cr_2O_7 = 8K_2CrO_4 + Cr_2O_3 + 6I.$$

The assumption that the decomposition is represented by the equation,

$$6KI + K_2Cr_2O_7 = 6I + 4K_2O + Cr_2O_3,$$

is quite erroneous.[1]

Lean and Whatmough[2] consider that the purest iodine is obtained by heating cuprous iodide.

When iodine is kept in a desiccator, the latter should contain calcium chloride and not sulphuric acid, and the cover should not be greased; neglect of these precautions leads to contamination of the iodine, since sulphuric acid is likely to be taken up by the iodine and grease is attacked by iodine vapours, forming hydriodic acid.

Meineke[3] prepares chemically pure iodine, for standardisation purposes, by precipitating a solution of equal parts potassium iodide and iodate with sulphuric acid. He subsequently recommended[4] the use of potassium bi-iodate, which had been previously suggested by C. v. Than;[5] the commercial form of this salt is said to be extremely pure and to be quite permanent, even in dilute solution. In acid solution the following reaction takes place :—

$$KH(IO_3)_2 + 10KI + 11HCl = 12\ I + 11\ KCl + 6H_2O.$$

Hence 390·1 parts of pure potassium bi-iodate correspond to 1523·6 parts iodine.

This method appears very convenient, particularly for checking thiosulphate solutions, from time to time, by means of a solution of the bi-iodate, but the purity of any commercial bi-iodate cannot be relied upon, as the salt may contain either too much or too little iodic acid. Experiments by Lunge,[6] with samples from the very best sources, gave results which would by no means warrant their use for direct standardisations, and their reliability was not improved by recrystallisation, either with or without the addition of free iodic acid. It was also observed that desiccation over sulphuric acid at ordinary temperatures, as recommended by J. Wagner, is insufficient, and that a temperature of 100° is required to dry the salt, as stated by Meineke; no appreciable decomposition results from this treatment. Treadwell[7] also states that commercial bi-iodate cannot be relied upon for direct standardisation. Hence, if it be desired to use potassium bi-iodate, its value must first be determined; this cannot be done directly by acidimetry (*cf.*

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[1] *Chem. Centr.*, 1903, **1**, 1435.

[2] *J. Chem. Soc.*, 1898, **73**, 148.

[3] *Chem. Zeit.*, 1892, **16**, 1219.

[4] *Ibid.*, 1895, **19**, 2.

[5] *Z. anal. Chem.*, 1877, **17**, 477.

[6] *Z. angew. Chem.*, 1904, **17**, 233.

[7] *Analytical Chemistry*, vol. ii., p. 509.

p. 89), so that sodium thiosulphate solution, standardised in some other way, must be resorted to. This negatives the value of bi-iodate for direct standardisations, and restricts its application to the occasional checking of thiosulphate, by means of a prepared solution of bi-iodate, the strength of which has been determined. Titration against pure iodine, as described on p. 118, is to be emphasised as the best method of standardisation, in spite of the many other proposals that have been put forward.

Riegler[1] has recommended crystallised iodic acid for standardising thiosulphate, but Walker[2] has pointed out objections to the method. Kratschmer[3] has suggested sodium bromate, Zulkowsky,[4] and subsequently Crismer,[5] normal potassium chromate, but Meineke[6] has indicated the disadvantages of this last reagent. J. Wagner[7] considers the use of potassium bichromate, under perfectly definite conditions, preferable to other reagents. Dietz and Margosches[8] use potassium chlorate, which, on addition of hydrochloric acid, potassium bromide, and potassium iodide, liberates an exactly equivalent amount of iodine.

$N/100$ thiosulphate is occasionally required, especially when using $N/100$ iodine; the former must always be freshly prepared, as it does not keep long. Neither is $N/10$ thiosulphate permanent under all conditions. Carbon dioxide acts upon it, in presence of oxygen and sunlight, forming sulphurous acid and free sulphur, and fungoid growths also develop. Topf,[9] after subjecting these changes to exact investigation, recommends that the solution be prepared with well-boiled water, free from carbon dioxide and stored in a cool place, protected from direct sunlight; a small quantity of potassium carbonate (*not* ammonium carbonate) should be added, but this necessitates addition of free acid to the iodine solution, when titrating. He further recommends that the solution be covered with a layer of petroleum ether, and that communication with the air be permitted only through an arrangement for absorbing carbon dioxide, the solution being withdrawn by means of a syphon. This proposal is probably rarely adopted, as it will be found preferable to check the strength of the solution about every two months.

Treadwell[10] states that all difficulties, due to the presence of carbon dioxide, etc., in preparing and storing thiosulphate solutions, may be overcome by dissolving the "pure" commercial salt in distilled water (even if it contains carbon dioxide) and allowing it to stand for at least a week (eight to fourteen days) before standardising. The carbon dioxide thus exhausts its action, a corresponding amount of sulphur

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[1] *Chem. Centr.*, 1897, **1**, 1169.

[2] *Z. anorg. Chem.*, 1898, **16**, 99.

[3] *Z. anal. Chem.*, 1885, **24**, 546.

[4] *J. prakt. Chem.*, 1868, **103**. 351.

[5] *Ber.*, 1884, **17**, 642.

[6] *Chem. Zeit.*, 1895, **19**, 3.

[7] *Z. angew. Chem.*, 1898, **11**, 951.

[8] *Ibid.*, 1903, **16**, 317; 1905, **18**, 1516.

[9] *Z. anal. Chem.*, 1887, **26**, 150.

[10] *Analytical Chemistry*, vol. ii., pp. 506 and 510.

separates, and the solution can then be kept for months without undergoing appreciable change. Ammonium carbonate should on no account be added to the solution.

Plimpton and Chorley[1] have recommended the use of barium thiosulphate for iodimetry; it is a very difficultly soluble salt. Mutniansky[2] has pointed out that a solution of this salt, saturated at 17°·5 C., is exactly centinormal.

ARSENIOUS ACID

An alkaline solution of arsenious oxide is unaffected by oxygen, but reacts with chlorine as follows:—

$$As_2O_3 + 4Cl + 5H_2O = 4HCl + 2H_3AsO_4.$$

Bromine and iodine act similarly, in alkaline solution. Hence, in many cases, arsenious acid solution may be used in place of sodium thiosulphate in conjunction with iodine; it has the advantage of being quite permanent. Its chief application is to the estimation of available chlorine in bleaching powder and in alkaline hypochlorites, the end-point of the reaction being ascertained by spotting on starch-iodide paper (*cf.* Bleaching powder, p. 503).

Pure, powdered, commercial arsenious oxide is used in preparing this solution; it should always be tested by subliming a small quantity from a dish on to a watch-glass; the first portion of the sublimate should not be yellowish, which would indicate the presence of the more easily volatile arsenious sulphide, and the whole should volatilise completely on heating more strongly. The oxide should be dried in the exsiccator over sulphuric acid for some time before use; it may then be weighed out without special precautions, as it is not hygroscopic.

To prepare a decinormal solution, exactly 4·950 g. arsenious oxide are weighed out and boiled with 10 g. pure sodium bicarbonate and 200 c.c. water, till completely dissolved; 10 g. of sodium bicarbonate are then added, the solution allowed to cool and diluted to 1 litre.

Reuter and Petriccioli[3] consider this method to be inaccurate, owing to the formation of sodium carbonate, which absorbs iodine, but Lunge[4] has shown that this objection lacks foundation, and that there is no reason for altering the method of preparing the solution as described.

The solution keeps perfectly; 1 c.c. is equivalent to 0·003545 g. chlorine, or 0·012697 g. iodine.

This solution will be of correct strength, provided pure dry arsenious oxide is used. It may be standardised, however, against pure iodine, exactly as described on p. 118, in connection with sodium thiosulphate,

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[1] *J. Chem. Soc.*, 1895, **67**, 315.

[2] *Zeit. anal. Chem.*, 1897, **36**, 220.

[3] *Z. angew. Chem.*, 1901, **14**, 1181.

[4] *Ibid.*, 1901, **14**, 1298.

and this check should not be omitted when a large quantity of solution is prepared.

Lunge[1] has shown that sodium arsenite and sodium thiosulphate give identical results and are equally applicable.

Silver Nitrate and Ammonium Thiocyanate

Silver nitrate solution is employed for the volumetric estimation of chlorides, by precipitation as silver chloride, using potassium chromate or sodium arsenate as indicator, in those cases in which rapidity is of greater importance than extreme accuracy; it is also applied to the estimation of cyanides. The method was introduced by F. Mohr. The preparation of this solution is extremely simple, as commercial crystallised silver nitrate is dry and chemically pure, and only requires to be dried in the desiccator, as a precaution, before being weighed out. A decinormal solution is obtained by dissolving 16·994 g. silver nitrate and making up to a litre; 1 c.c. of this solution is equivalent to 0·003545 g. Cl, 0·003645 g. HCl, 0·005850 g. NaCl, etc.

A solution equivalent to 0·001 g. NaCl per c.c. is sometimes preferred; this is obtained by dissolving 2·906 g. silver nitrate per litre of solution.

The solutions to be estimated must not contain any free acid; if this is present, it must be neutralised by sodium carbonate. A slight excess of carbonate is immaterial, whilst the least excess of acid interferes with the reaction. Four to five drops of a cold, saturated solution of normal (yellow) potassium chromate are added to the chloride solution, and the silver solution is then run in, with vigorous stirring, until the white precipitate has acquired a reddish colour, which does not disappear on stirring; the colour is seen even better by artificial light than in daylight, as the yellow colour of the solution is not apparent, whilst the red of the precipitate persists. With a decinormal silver nitrate solution an excess of about 0·2 c.c. is required; this amount must be subtracted from the quantity of solution used. The colour change is sharper when sodium arsenate is used as indicator, and a correction for excess is unnecessary. A titration which has been carried too far can be corrected by addition of $N/10$ sodium chloride solution.

Volhard's[2] method permits the use of acid solutions. A solution of ammonium thiocyanate is required in addition to $N/10$ silver nitrate; this is prepared by dissolving 7·5 to 8 g. of the salt, which is always moist, in 1 litre of solution and accurately adjusting it to the silver nitrate solution. Once standardised, the titre remains perfectly constant. A solution of iron alum (ferric ammonium sulphate), saturated at the ordinary temperature, serves as indicator; 5 c.c. of this are

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[1] *Z. angew. Chem.*, 1904, **17**, 233.

[2] *Annalen*, 1878, **190**, 49.

added to from 200 to 300 c.c. of the solution to be titrated. To fix the strength of the thiocyanate solution, 10 or 20 c.c. silver nitrate solution are diluted with 200 c.c. water, and 5 c.c. iron alum solution are added; if a colour develops, nitric acid is added until it disappears. The thiocyanate solution is then run into the silver solution, with continual stirring; the appearance of a light-brown coloration indicates the end-point of the reaction, and its observation is facilitated by the coagulation of the silver thiocyanate. Henriques has pointed out that the thiocyanate must always be run into the silver solution, not *vice versa*. The thiocyanate solution thus tested is corrected and made up to decinormal strength, as described on p. 86. For chloride estimations, the solution to be analysed is treated with $N/10$ silver nitrate until all the chlorine is precipitated as silver chloride and excess of silver nitrate is present; iron alum is then added and the excess of silver titrated back with $N/10$ thiocyanate. The amount of chloride is given by the difference between the volumes of silver nitrate and of thiocyanate solutions used.

General Remarks on Volumetric Analysis

Correct illumination is important in almost all volumetric work, to ensure the recognition of colour changes such as are produced by the addition of a single drop of solution. Direct sunshine may be as harmful as the insufficient light of a dull winter's day, or of an unsuitable position in the laboratory. Wherever possible, the burettes should be placed opposite a window, preferably with a north light, even if only to facilitate the reading. Colour changes, especially that of litmus, are generally less distinct in artificial light; yellow light is particularly objectionable in this respect, but incandescent gas light or electric light are nearly as good as daylight, after some experience has been gained with these illuminants.

In all cases a pure white background should be placed immediately under the vessel in use and spread over a considerable area of the bench. The nicest and cleanest arrangement is a tiled bench, but a sheet of white paper is almost as serviceable.

In order to be sure, in doubtful cases, whether a colour change has really occurred or not, the flask should be observed by both reflected and transmitted light, and it should also be looked at from the side and from above. A beginner will frequently find it advantageous to have two other vessels, of the same size as the titration vessel ready to hand, each filled with a solution coloured to the same intensity as the solution to be titrated, and in one of which the colour change has been effected. These considerations apply to most colorimetric work.

It is generally advisable, in cases of uncertainty in colour changes, to read the burette and then to add a further drop of the solution; if only the intensity of the colour changes and not its shade, this last drop should not be reckoned in the titration. It is frequently more certain to titrate, drop by drop, until the change has become quite definite, and then to determine the exact end-point by titrating back with the appropriate standard solution.

The liquid should be agitated during the titration, especially towards the end of the reaction. It is better to shake the vessel well than to stir with a glass rod, as the falling drops may easily splash off the latter. A beaker can be shaken in this way without fear of loss, provided it is not more than half full, but it is better to use an Erlenmeyer flask with a short, wide neck. Narrow-mouthed flasks are not convenient, as drops from the burette may fall outside.

The importance of the quality of glass has been previously discussed (p. 54).

When a solution has to be boiled in a porcelain dish, the dish should on no account be more than half full; otherwise the spitting of the solution may easily be a source of loss.

H. Gas-Volumetric Analysis

Gas-volumetric analysis, as distinct from gas analysis, comprises those operations in which a constituent of a solid or liquid substance is determined by the generation and measurement of a gas. The gas is usually evolved by the decomposition of the substance under examination; for instance, carbon dioxide from limestone, nitrogen from ammonium salts, nitric oxide from nitrates, oxygen from peroxides, etc.; sometimes, however, it is partially or entirely generated from the reagent used, as in the valuation of hydrogen peroxide by potassium permanganate or of zinc-dust, by means of hydrogen liberated from water.

In some instances, air displaced by the generated gas is measured instead of the latter.

The description of the methods and forms of apparatus proposed for gas-volumetric work is, in this section, restricted to such as are employed for a number of different purposes and are in general laboratory use. Those forms of apparatus which are either used only for a special purpose, or in connection with a particular industry, are described in the corresponding sections.

The calibration of gas-volumetric apparatus has already been considered (p. 44).

The Azotometer.

This instrument was designed by Knop[1] for the determination of ammonia, by the decomposition of its salts with sodium hypobromite,

[1] *Chem. Centr.*, 1860, **5**, 244. *Z. anal. Chem.*, 1874, **13**, 383; 1876, **15**, 250.

and measurement of the liberated nitrogen. It has been improved in several respects, especially by P. Wagner,[1] and can be used for other gas-volumetric purposes in which measurements are made over water, as has been recommended by A. Baumann (1890) and others.

The apparatus is shown in Fig. 40. A is a generating vessel for holding the hypobromite solution. This is prepared as follows:—100 g. sodium hydroxide are dissolved in water and diluted to 1·25 litres, 25 c.c. bromine are added, with external cooling by water, the whole well shaken, and finally cooled. The solution is kept in the dark in a well-stoppered bottle. The glass cylinder *a*, of about 20 c.c. capacity, is fused on to the bottom of A, and serves to hold the solution of the ammonium salt. The large glass vessel B, which has a capacity of about 4 litres, is for cooling the generating vessel to its original temperature, after the decomposition. The neck of the generating vessel is rough-ground inside, so as to give a good hold for the rubber

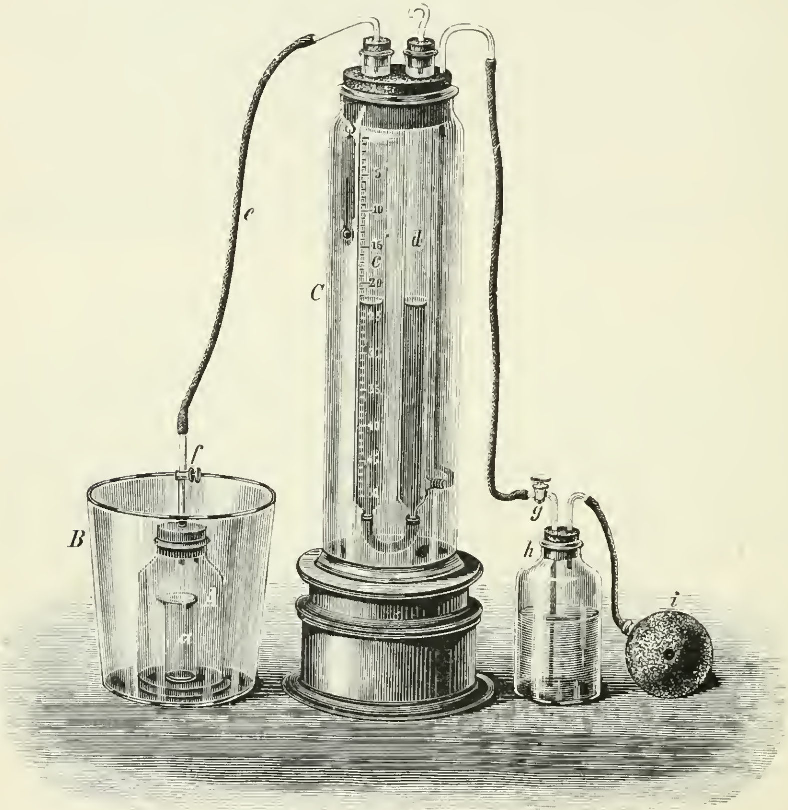

FIG. 40.

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[1] *Z. anal. Chem.*, 1870, **9**, 225; 1875, **14**, 247.

stopper, which must be pressed in tightly, and must not slip. C is a tall cylinder filled with water (to which a little hydrochloric acid is added to prevent the growth of moulds), and closed by a cork in which the communicating burettes, *c* and *d*, are fixed, and carrying a small thermometer. The burettes and their supply vessel *h* are filled with water, which may be slightly coloured.

By following the subjoined instructions of P. Wagner[1] carefully, ammoniacal nitrogen can be very accurately determined with this instrument. 10 c.c. of the ammonium salt solution under examination are introduced into the inner vessel *a*, and 50 c.c. of hypobromite solution into the outer vessel A, by means of a funnel. The rubber stopper is then tightly inserted and the vessel placed in B, which is filled with water. The glass tap *f* is loosened slightly, water introduced into the burettes *c* and *d* by squeezing the rubber ball *i* and opening the tap *g*, and then run off through *g* down to the zero mark of the burette. After about ten minutes the cock *f*, which is slightly greased, is inserted tightly, but left open so that A and *c* are in communication. If, after an interval of five minutes, the liquid in *c* has risen, the cock *f* is again loosened, re-inserted tightly, and the apparatus again allowed to stand for five minutes. If the liquid has remained at the zero mark, the temperature of the generating vessel and contents has become equal to that of the surrounding water, and no more carbon dioxide, from the enclosed air, is being absorbed by the hypobromite solution.

To carry out the decomposition, 30 to 40 c.c. of water are first withdrawn from the burette through *g*, and the generating vessel removed from B and tilted, so that a small portion of the contents of *a* flow into the hypobromite solution, with which they are mixed by gentle shaking. This is repeated until the greater portion of the ammoniacal liquid has been poured out and decomposed. The tap *f* is then closed, the generating vessel thoroughly shaken, *f* again opened to allow any liberated nitrogen to pass to the burette, and this repeated until the liquid in *c* remains at a constant level; shaking three times is usually sufficient. The generating vessel A is then replaced in B; fifteen to twenty minutes suffice for this vessel and its contents to acquire the temperature of the surrounding water and for the gas in *c* to reach that of the water-jacket C, which is indicated by the thermometer. The tap *g* is then opened until the water is at the same level in *c* and *d*, and the volume of liberated nitrogen, the temperature of the water in C, and the barometric pressure noted. The weight of nitrogen may then be calculated from the following tables prepared by Dietrich (pp. 128-130).

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[1] *Lehrbuch der Düngerfabrikation*, 1877, p. 161.

I.—Dietrich's Table for the Absorption of Nitrogen.

In 60 *c.c. generating liquid* (50 *c.c. hypobromite solution and* 10 *c.c. water*), *the hypobromite solution having the sp. gr.* 1·1, *and of such strength that* 50 *c.c. correspond to* 200 *mg. N when from* 1 *to* 100 *c.c. of gas are evolved.*

Liberated . .	1	2	3	4	5	6	7	8	9	10
Absorbed . .	0·06	0·08	0·11	0·13	0·16	0·18	0·21	0·23	0·26	0·28
Liberated . .	11	12	13	14	15	16	17	18	19	20
Absorbed . .	0·31	0·33	0·36	0·38	0·41	0·43	0·46	0·48	0·51	0·53
Liberated . .	21	22	23	24	25	26	27	28	29	30
Absorbed . .	0·56	0·58	0·61	0·63	0·66	0·68	0·71	0·73	0·76	0·78
Liberated . .	31	32	33	34	35	36	37	38	39	40
Absorbed . .	0·81	0·83	0·86	0·88	0·91	0·93	0·96	0·98	1·01	1·03
Liberated . .	41	42	43	44	45	46	47	48	49	50
Absorbed . .	1·06	1·08	1·11	1·13	1·16	1·18	1·21	1·23	1·26	1·28
Liberated . .	51	52	53	54	55	56	57	58	59	60
Absorbed . .	1·31	1·33	1·36	1·38	1·41	1·43	1·46	1·48	1·51	1·53
Liberated . .	61	62	63	64	65	66	67	68	69	70
Absorbed . .	1·56	1·58	1·61	1·63	1·66	1·68	1·71	1·73	1·76	1·78
Liberated . .	71	72	73	74	75	76	77	78	79	80
Absorbed . .	1·81	1·83	1·86	1·88	1·91	1·93	1·96	1·98	2·01	2·03
Liberated . .	81	82	83	84	85	86	87	88	89	90
Absorbed . .	2·06	2·08	2·11	2·13	2·16	2·18	2·21	2·23	2·26	2·28
Liberated . .	91	92	93	94	95	96	97	98	99	100
Absorbed . .	2·31	2·33	2·36	2·38	2·41	2·43	2·46	2·48	2·51	2·53

II.—Dietrich's Table for the Weight of 1 c.c. of Nitrogen.

In Milligrams, at pressures from 720 to 770 Millimetres of Mercury, and Temperatures from 10° to 25° C.

Temp. in degrees Centigrade.	Millimetres.												
	720	722	724	726	728	730	732	734	736	738	740	742	744
10	1·13380	1·13699	1·14018	1·14337	1·14656	1·14975	1·15294	1·15613	1·15932	1·16251	1·16570	1·16889	1·17208
11	1·12881	1·13199	1·13517	1·13835	1·14153	1·14471	1·14789	1·15107	1·15424	1·15742	1·16060	1·16378	1·16696
12	1·12376	1·12693	1·13010	1·13326	1·13643	1·13960	1·14277	1·14593	1·14910	1·15227	1·15543	1·15860	1·16177
13	1·11875	1·12191	1·12506	1·12822	1·13138	1·13454	1·13769	1·14085	1·14401	1·14716	1·15032	1·15348	1·15663
14	1·11369	1·11684	1·11999	1·12313	1·12628	1·12942	1·13257	1·13572	1·13886	1·14201	1·14515	1·14830	1·15145
15	1·10859	1·11172	1·11486	1·11799	1·12113	1·12426	1·12739	1·13053	1·13366	1·13680	1·13993	1·14306	1·14620
16	1·10346	1·10658	1·10971	1·11283	1·11596	1·11908	1·12220	1·12533	1·12845	1·13158	1·13470	1·13782	1·14095
17	1·09828	1·10139	1·10450	1·10761	1·11073	1·11384	1·11695	1·12006	1·12317	1·12629	1·12940	1·13251	1·13562
18	1·09304	1·09614	1·09924	1·10234	1·10544	1·10854	1·11165	1·11475	1·11785	1·12095	1·12405	1·12715	1·13025
19	1·08774	1·09083	1·09392	1·09702	1·10011	1·10320	1·10629	1·10938	1·11248	1·11557	1·11866	1·12175	1·12484
20	1·08246	1·08554	1·08862	1·09170	1·09478	1·09786	1·10094	1·10402	1·10710	1·11018	1·11327	1·11635	1·11943
21	1·07708	1·08015	1·08322	1·08629	1·08936	1·09243	1·09550	1·09857	1·10165	1·10472	1·10779	1·11086	1·11393
22	1·07166	1·07472	1·07778	1·08084	1·08390	1·08696	1·09002	1·09308	1·09614	1·09921	1·10227	1·10533	1·10839
23	1·06616	1·06921	1·07226	1·07531	1·07836	1·08141	1·08446	1·08751	1·09056	1·09361	1·09666	1·09971	1·10276
24	1·06061	1·06365	1·06669	1·06973	1·07277	1·07581	1·07885	1·08189	1·08493	1·08796	1·09100	1·09404	1·09708
25	1·05499	1·05801	1·06104	1·06407	1·06710	1·07013	1·07316	1·07619	1·07922	1·08225	1·08528	1·08831	1·09134

Dietrich's Table for the Weight of 1 *c.c. of Nitrogen*—Continued.

Temp. in degrees Centigrade.	Millimetres.												
	746	748	750	752	754	756	758	760	762	764	766	768	770
10	1·17527	1·17846	1·18165	1·18484	1·18803	1·19122	1·19441	1·19760	1·20079	1·20398	1·20717	1·21036	1·21355
11	1·17014	1·17332	1·17650	1·17968	1·18286	1·18603	1·18921	1·19239	1·19557	1·19875	1·20193	1·20511	1·20829
12	1·16493	1·16810	1·17127	1·17444	1·17760	1·18077	1·18394	1·18710	1·19027	1·19344	1·19660	1·19977	1·20294
13	1·15979	1·16295	1·16611	1·16926	1·17242	1·17558	1·17873	1·18189	1·18505	1·18820	1·19136	1·19452	1·19768
14	1·15459	1·15774	1·16088	1·16403	1·16718	1·17032	1·17347	1·17661	1·17976	1·18291	1·18605	1·18920	1·19234
15	1·14933	1·15247	1·15560	1·15873	1·16187	1·16500	1·16814	1·17127	1·17440	1·17754	1·18067	1·18381	1·18694
16	1·14407	1·14720	1·15032	1·15344	1·15657	1·15969	1·16282	1·16594	1·16906	1·17219	1·17531	1·17844	1·18156
17	1·13873	1·14185	1·14496	1·14807	1·15118	1·15429	1·15741	1·16052	1·16365	1·16674	1·16985	1·17297	1·17608
18	1·13335	1·13645	1·13955	1·14266	1·14576	1·14886	1·15196	1·15506	1·15816	1·16126	1·16436	1·16746	1·17056
19	1·12794	1·13103	1·13412	1·13721	1·14030	1·14340	1·14649	1·14958	1·15267	1·15576	1·15886	1·16195	1·16504
20	1·12251	1·12559	1·12867	1·13175	1·13483	1·13791	1·13999	1·14408	1·14716	1·15024	1·15332	1·15640	1·15948
21	1·11700	1·12007	1·12314	1·12621	1·12928	1·13236	1·13543	1·13850	1·14157	1·14464	1·14771	1·15078	1·15385
22	1·11145	1·11451	1·11757	1·12063	1·12369	1·12675	1·12982	1·13288	1·13594	1·13900	1·14296	1·14512	1·14818
23	1·10581	1·10886	1·11191	1·11496	1·11801	1·12106	1·12411	1·12716	1·13021	1·13326	1·13631	1·13936	1·14241
24	1·10012	1·10316	1·10620	1·10924	1·11228	1·11532	1·11835	1·12139	1·12443	1·12747	1·13051	1·13355	1·13659
25	1·09437	1·09740	1·10043	1·10346	1·10649	1·10952	1·11255	1·11558	1·11861	1·12164	1·12467	1·12770	1·13073

Example of calculation:

Volume of liberated nitrogen . .	22 c.c.
Temperature	16°
Barometric pressure . . .	756 mm.

Then, according to Table I., 0·58 c.c. nitrogen remain dissolved in the generating liquid, and according to Table II., the weight of 1 c.c. of nitrogen at 16° and 756 mm. pressure is 1·15969 mg. The weight of nitrogen in the substance examined is therefore:—

$$(22.0 + 0.58) \times 1.15969 = 26.19 \text{ mg.}$$

These tables are given as they are in very general use; they do not, however, possess any special advantages, nor are they based on the correct value for the weight of 1 c.c. of nitrogen (cf. *infra*).

Lunge[1] has shown that it is unnecessary to use Table I. to correct for the so-called "absorption of nitrogen," which is really due to incomplete reaction, and that it suffices to add 2·5 per cent. to the volume of gas found. This calculation may be simplified by using

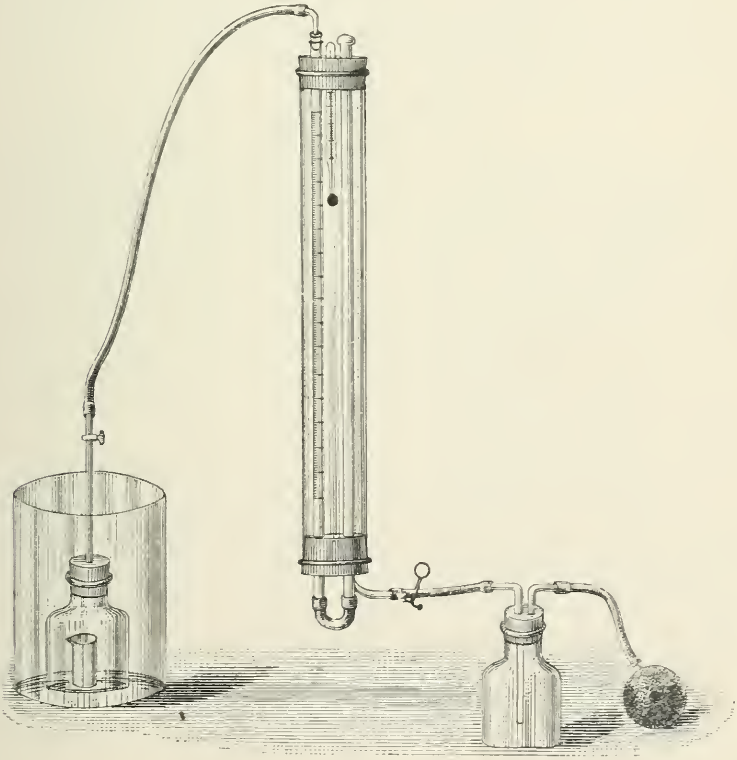

Fig. 41.

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[1] *Chem. Ind.*, 1885, 5, 165.

the increased factor 0·001558 to convert each c.c. of nitrogen at 0° C. and 760 mm. (dry) into grams of ammonia. This factor is calculated from the observed density of nitrogen.

A. Baumann recommends the simplified form of Wagner's Azotometer shown in Fig. 41, for technical laboratories, in which the measuring tube is replaced by an ordinary pinch-cock burette; the manipulation of the apparatus is in all respects similar to that described above. If many analysis have to be performed it is well to keep two or three such simplified azotometers in use, so as to save time whilst the original temperature is being attained, after the decompositions.

It is particularly important, when using the azotometer, that the temperature in the generating vessel and measuring tube should remain constant during the whole experiment. If the capacity of the former is only 150 c.c. a temperature variation of 1° C. causes an error of 0·5 c.c., and one of 2° C. of about 1 c.c. Such errors influence the result of the analysis considerably, especially when small quantities of gas are liberated, amounting, for instance, to 5 to 10 per cent. of the total volume when 10 c.c. of gas are evolved.

The Nitrometer.

The name "Nitrometer" was given by Lunge[1] to the apparatus he devised for the determination of nitrogen acids, by decomposition with sulphuric acid, in presence of mercury. This reaction was made use of long ago by W. Crum[2] for the analysis of nitrates and of gun-cotton, and subsequently, in an improved form, by Frankland and Armstrong[3] for the determination of nitrates in water, and by G. E. Davis[4] for the valuation of nitrous vitriol, but manipulative difficulties restricted its applicability; the nitrometer has rendered the reaction thoroughly practicable, and has thus been the means of bringing it into general use.

In the method as originally devised, the mercury over which the gas is collected also takes part in the reaction. It has since been extended to many other purposes, in which the mercury does not take part in the decomposition, but serves simply as the confining liquid for the liberated gas, and also to determinations in which the decomposition is effected in a separate vessel and the evolved nitric oxide collected and measured, over dry mercury, in the nitrometer. Various alterations have thus been made in the original apparatus from time to

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[1] *Ber.*, 1878, **11**, 174; 1885, **18**, 1878 and 2030 (New applications); 1888, **21**, 376. *Dingl. polyt. J.*, 1879, **231**, 522 (Tables); 1882, **245**, 171 (Analysis of dynamite). *Chem. Ina.*, 1881, **4**, 346; 1885, **8**, 161 (New applications); 1886, **9**, 273 (Analysis of explosives). *J. Soc. Chem. Ind.*, 1882, **1**, 15; 1885, **4**, 495; 1886, **5**, 82; 1888, **7**, 232; 1892, **11**, 778. *Sulphuric Acia and Alkali*, 2nd edition, 1891, p. 182. *Cf.* also A. H. Allen, *J. Soc. Chem. Ind.*, 1885, **4**, 178.

[2] *Phil. Mag.*, 1847, [3], **30**, 426.

[3] *Chem. Soc.*, 1868, **21**, 101.

[4] *Chem. News*, 1878, **37**, 45.

time; the literature is given in the above references. The "gas-volumeter," which was developed by Lunge from the nitrometer, will be described subsequently.

The very extended applicability of the nitrometer is mainly due to the following reasons. In the first place, most gases, even those which are soluble to a considerable extent in water, can, by its means, be measured over mercury without the use of a mercury trough, which previously was always necessary for this purpose, and the apparatus is simple, requires but little mercury, and is easy to manipulate and to shake; secondly, it is equally suitable, either for those cases in which a gas is evolved and measured in the pure state, or for those in which it is liberated in a separate vessel and the displaced air measured. It can also be used for ordinary gas analysis, and for determinations in which a gas, generated from a solid or liquid substance, has to be separated from other gases, as in the determination of carbon dioxide by Lunge and Marchlewski's method, etc.

Böckmann,[1] in describing the nitrometer, says:—

"Lunge's nitrometer, in its various modifications, is an exceptionally valuable apparatus, and is therefore very largely used for technical work. There is scarcely another apparatus for technical analysis which has so many practical applications and is at the same time so easily handled. Those of its applications which have been published are numerous; those which are unpublished, and which are carried on in almost every technical laboratory, are certainly still more numerous."

The nitrometer is shown in Fig. 42 in its original form, as still used in most cases for the analysis of nitrous vitriol in the sulphuric acid industry, and for many other purposes. The tube *a* has a capacity of 50 c.c.; it is drawn out at the bottom and is graduated in $\frac{1}{10}$ c.c. The graduations start immediately below the three-way tap which terminates the tube at the top. This tap may either have a vertical and an axial passage, as in Winkler's or Bunté's gas-burettes, or it may be a Friedrich-Greiner tap with two oblique passages, as shown in its three positions in Fig. 43. The latter form closes more tightly and is more easily manipulated than the former, and is there-

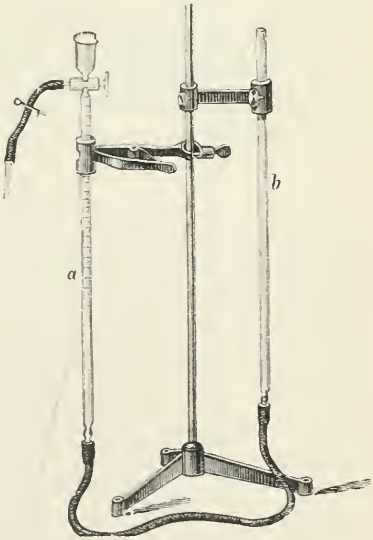

Fig. 42.

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[1] Third edition, I, 63-64.

fore usually attached to the newer forms of the apparatus. Above the tap, a beaker and a side tube *d* are attached ; the latter replaces the axial passage of the older form of tap. In position A the measuring tube communicates with the side tube *d*, in position B with the beaker, and in position C the tap is closed.

The measuring tube *a* (Fig. 42) is connected by means of thick-walled rubber tubing with the pressure tube *b*. The latter is a simple cylindrical glass tube of the same diameter as the measuring tube, and drawn out at the bottom for the attachment of the rubber tubing. Both tubes are held by clamps, in which they can be moved.

To use the apparatus, for instance for the assay of nitrous vitriol, the tube *b* is placed so that its lower end is somewhat higher than the tap on *a*, and mercury is poured in through *b*, the tap on *a* being open, until it enters the beaker on *a* ; as the mercury enters *a* from below, no air-bubbles are formed on the sides of the tube. The tap is then closed, the mercury in the beaker allowed to flow out through the side passage of the tap, the pressure tube lowered, and the tap closed.

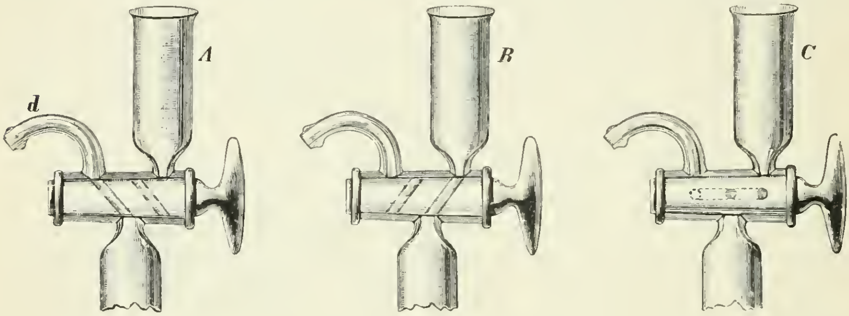

FIG. 43.

The nitrous vitriol is then introduced into the beaker from a 1 c.c. pipette divided into $\frac{1}{100}$ c.c. ; in the case of very strong nitrous vitriol 0·5 c.c. are used, in other cases 2 to 5 c.c. The pressure tube *b* is then lowered, the tap carefully opened, and the acid drawn into the measuring tube, care being taken not to admit any air. The beaker is then rinsed with 2 to 3 c.c. of sulphuric acid, free from nitrogen acids, which is similarly drawn into the measuring tube, and the washing repeated with 1 to 2 c.c. more of sulphuric acid. The decomposition is then started by removing the tube *a* from its clamp, and thoroughly mixing the acid and mercury by repeatedly holding the tube almost horizontally, taking care that no acid gets into the rubber tubing, and then sharply raising it to a vertical position. The tube is shaken for one to two minutes until no more gas is evolved.

The two tubes are then placed so that the mercury in *b* is as much higher than that in *a* as is necessary to compensate for the layer of acid in the latter; 1 mm. mercury is allowed for every 6½ mm. of acid. After the temperature has become equalised the pressure is exactly adjusted by pouring a little acid into the beaker and opening the tap cautiously. If the gas is under diminished pressure, which is preferably the case, acid will flow into *a*; the tap is at once closed before air can enter, and the operation repeated after raising the pressure tube very slightly. If, on the contrary, the enclosed gas tends to force its way through the acid, the tap is closed, the pressure tube lowered slightly, and the tap again opened. With a little care these manipulations can always be successfully carried out. The volume of the gas, the barometric pressure, and the temperature are then read; the latter by means of a thermometer, the bulb of which is placed close to the measuring tube and near the middle of the column of gas.

When the determination is finished the measuring tube *a* is lowered, so that no air may enter on opening the tap, and the gas expelled by raising the pressure tube. The acid is expelled, either through the side tube *d* (Fig. 43), or through the axial passage in the older form of tap, and the last traces removed with filter paper. The nitrometer is then ready for the next determination.

It is always necessary to make sure that the tap of the nitrometer fits tightly, and this is best secured by greasing it with a little vaseline; care must be taken that no vaseline gets inside the tap and so comes into contact with the acid, as this causes the formation of froth, which only settles very slowly.

A glass tap can hardly be expected to keep perfectly closed, for any length of time, when exposed to considerable variations of pressure; the tap can, however, be regarded as satisfactory if no air enters the measuring tube during an interval of two hours after it has been completely filled with mercury and the pressure tube lowered. Details with regard to the calculation of the amount of nitrogen compounds from the volume of gas obtained are given in the section "Sulphuric Acid."

The analysis of nitrates or of nitrites soluble in water, to determine the total nitrogen, is carried out similarly, as is described in connection with the analysis of sodium nitrate. In such cases, where a solid, soluble in water, is to be analysed, the weighed substance is introduced into the beaker, dissolved there in a very small quantity of water, the solution drawn into the measuring tube, the beaker rinsed with concentrated sulphuric acid, and the decomposition carried out as described.

In the analysis of substances insoluble in water but soluble in strong sulphuric acid, more especially dynamites and pyroxylins, for which purpose the nitrometer is now almost always used, the solution in sulphuric acid is also carried out in the attached beaker. In this case, in order to avoid loss of nitrous fumes, the device shown in Fig. 44, due to Lunge,[1] is used. The beaker of the nitrometer is closed by a rubber stopper provided with an S-tube, ending above in a small funnel. The substance is placed in the beaker, and concentrated sulphuric introduced through the funnel. The lower bend of the tube naturally remains full of sulphuric acid, which prevents the escape of nitrous fumes, and which flows into the beaker, as the acid in the latter is drawn into the measuring tube.

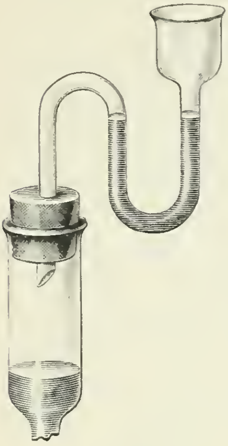

FIG. 44.

It is immaterial whether an insoluble powder, such as kieselguhr in the case of dynamite, or some undissolved saltpetre, etc., remains, as this is sucked into the measuring tube with the liquid; in the analysis of pyroxylin it is, however, better to wait till it has completely dissolved in the beaker.

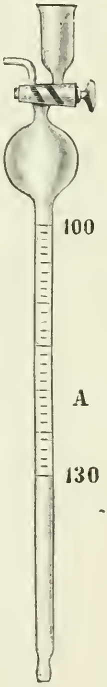

FIG. 45.

FIG. 46.

Nitrates and esters of nitric acid, such as nitroglycerine and nitrocellulose, can be analysed in the apparatus shown in Fig. 42, but a high degree of accuracy is not obtainable, as not more than 40 c.c. of gas can be measured. By using a modified form, the "nitrometer for saltpetre," shown in Fig. 45, an accuracy of 0·1 per cent., which is not surpassed by that of any other method, may be obtained in these determinations. In this form a larger space for gas is provided without making the apparatus inconveniently long, by means of a bulb of nearly 100 c.c. capacity, below which the graduations extend from 100 c.c. to 130 c.c.

In Fig. 46 a form of nitrometer is shown which may be used for determinations in which either a small or a large volume of gas is evolved. As it cannot be made so short as the forms shown in Figs. 42 and 45, it is not so suitable for shaking, but it is well adapted for use in conjunction with a decomposition bottle or as a gas-volumeter (cf. *infra*).

When nitrous and nitric acid compounds are decomposed by shaking in the measuring tube itself with mercury and sulphuric acid, a layer of sulphuric acid finally remains between the gas and the mercury, which

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[1] *Chem. Ind.*, 1886, 9, 274.

has to be allowed for in adjusting the pressure for the final measurement, as stated above. This causes no special difficulty as a rule, but when considerable quantities of substance are decomposed, much frothing sometimes occurs; on dilution with water, which is, in some cases, unavoidable, sulphate of mercury is precipitated, and in the analysis of dynamite the kieselguhr floats on the top of the acid, etc. These factors make the final adjustment and measurement uncertain and inexact. In such cases, for instance in the analysis of saltpetre and of explosives, it is therefore advisable to use a separate decomposition vessel, with an attached pressure tube, as in the gas-volumeter. The gas is then always measured over a sharp meniscus, and the volume can be read with the greatest accuracy.

The same considerations apply to all those methods of analysis in which the nitrometer is used in conjunction with an attached decomposition bottle, as shown in Fig. 47. The manipulation is then identical with that of the azotometer. The substance to be decomposed is placed in the outer annular space, and the decomposing agent in the inner vessel, which is fused on to the bottom of the bottle. After replacing the stopper, the bottle is connected with the tap of the nitrometer, the measuring tube of which has been completely filled with mercury; the stopper is again loosened, to make sure that there is no excess of pressure in the generating bottle, and the mercury in the nitrometer re-adjusted to zero, if necessary, by moving the pressure tube. The tap of the nitrometer is then turned so as to connect the measuring tube and the generating bottle, and the latter tilted, so that the liquid in the inner vessel flows into the surrounding space. In doing this care must be taken that the bottle is not warmed by the hand, and this applies also to the subsequent shaking, to promote the disengagement of the gas; it is safest, especially if heat is evolved, as in decompositions by the sodium hypobromite method, to place the generating bottle up to the neck in a beaker of water, before and after the

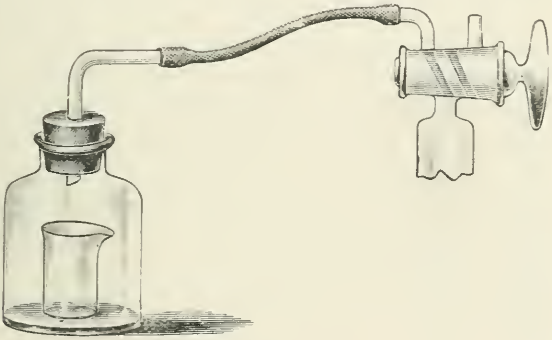

FIG. 47.

reaction As the mercury in the measuring tube is depressed by the evolved gas, the pressure tube is lowered accordingly, to prevent any excessive pressure; it is sometimes advantageous to lower the pressure tube considerably towards the end of the reaction, in order to facilitate the removal of the gas. After the original temperature has been attained the mercury is brought to the same level in both tubes, and the volume of the gas read, together with the temperature and pressure, as described on p. 135.

In reducing to 760 mm. pressure, it must be borne in mind that the gas is moist, and not dry, as is usually the case in working with a nitrometer; since it is always generated from dilute solutions, the tension of the water-vapour may be considered equal to that of pure water at the same temperature.

The reduction of the volume of gas to normal volume is calculated most easily by means of the Tables VI. to VIII., appended to this volume, which were specially compiled for use with the nitrometer by Lunge; the calculation can also be done by reversing the formulæ on p. 140.

The numerous applications of this form of the nitrometer include the valuation of potassium permanganate solution (p. 109), the analysis of bleaching powder, manganese dioxide, potassium ferricyanide, lead peroxide, nitrous acid,[1] hydrogen peroxide, the determination of carbon dioxide in carbonates (preferably by Lunge and Marchlewski's method), of nitrogen in ammonium salts, in urea (ureometer), and in diazo-compounds, the control of the strength of acids by liberation of carbon dioxide from carbonates, the valuation of zinc-dust, the examination of chromates[2] and the titration of iodine solutions[3] (*cf.* p. 114).

The nitrometer can also be used as an absorptiometer,[4] as an apparatus for reducing the volume of gases to 0° and 760 mm. pressure,[5] although the gas-volumeter is far preferable for this purpose, and for most gas-analytical work;[6] also for the collection and analysis of gases dissolved in water, etc.[7]

The Gas-Volumeter.[8]

This name was given by Lunge to an apparatus, by means of which the reduction of a volume of gas, either wet or dry, to any required normal conditions, usually, of course, to 0° and 760 mm. pressure, is effected without observation of the temperature and

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[1] Riegler, *Z. anal. Chem.*, 1897, **36**, 665.

[2] A. Baumann, *Z. angew. Chem.*, 1891, **4**, 135, 198, 339, 392.

[3] *Z. angew. Chem.*, 1891, **4**, 203, 328, 450.

[4] *Chem. Ind.*, 1885. **8**, 162.

[5] *Ibid.*, 1885, **8**, 163.

[6] *Ibid.*, 1885, **8**, 169.

[7] *Ibid.*, 1885, **8**, 170; *Z. anal. Chem.*, 1886, **25**, 309.

[8] Lunge, *Ber.*, 1890, **23** 440; 1892, **25**. 3157. *Z. angew. Chem.*, 1890, **3**, 139; 1891, **4**, 197, 410; 1892, **5**, 677. *J. Soc. Chem. Ind.*, 1890, **9**. 547.

pressure, and without calculation or reference to tables. This operation, which is necessary in all gas-volumetric work, can be performed by means of this instrument, in less than a minute, in a purely mechanical manner, and is applicable, not merely for relative measurements, but also for absolute measurements, such as are required in the analysis of solid and liquid substances, by gas-volumetric methods.

The principle of the apparatus is to enclose a known volume of air, at such a pressure that it takes up exactly the volume which it would occupy at 0° and 760 mm. pressure. If the same pressure and temperature are then applied to another volume of gas, this will also take up the volume which it would occupy at 0° and 760 mm. pressure. This condition is attained by confining the known volume of air in a "reduction tube" to which a pressure tube is attached, and placing the latter in such a position that the gas in the reduction tube is brought to the volume it would occupy under normal conditions; the reduction tube is also connected with the gas measuring tube by means of a T-piece, and by adjusting the level of the mercury in the two tubes to the same height, the volume correction is applicable directly to the gas in the measuring tube.

The apparatus is shown in Fig. 48. The three tubes, A, B, and C, are connected by means of a T-piece and sufficiently long thick rubber tubing, and are held to a stand by clamps, in which they can be moved in a vertical direction. The tube A is the measuring tube, and may be a nitrometer of any form, a Bunté burette, or any other apparatus for the measurement of gases. The second tube, B, the so-called reduction tube, is enlarged to a bulb at the top; the first graduation is below the widened portion of the tube, and indicates a volume of 100 c.c., and the lower cylindrical portion of the tube is graduated in $\frac{1}{10}$ c.c. for another 30 to 40 c.c. The tube is set, once for all, by observing the temperature and pressure, calculating the

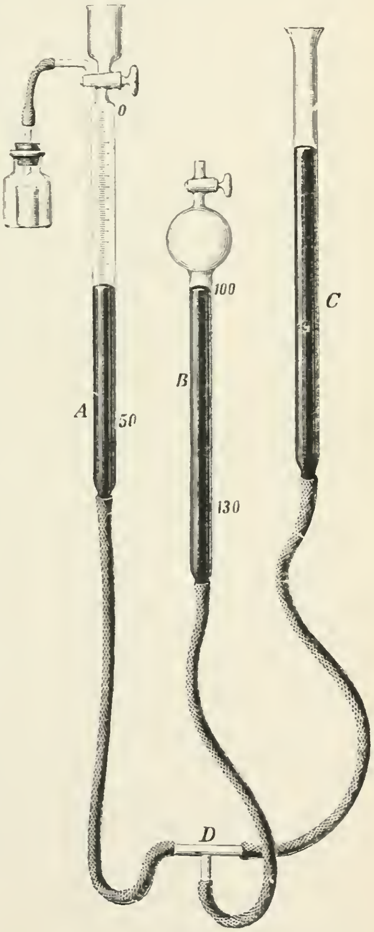

Fig. 48.

volume which 100 c.c. of dry air would occupy under the observed conditions, bringing the mercury to the corresponding division, and closing the tap above the bulb. If the tap is air-tight the reduction to 0° and 760 mm. pressure has been permanently made; an alternative is to provide the upper end of the tube with a capillary, which can be sealed off, after the volume has been correctly adjusted.

This form of reduction tube was subsequently modified by Lunge and replaced by the cylindrical form shown in Fig. 52 (p. 144), in order to bring the volumes of enclosed gas as far as possible into a parallel position. Both the simple tap shown in Fig. 48 and a sealed capillary have certain disadvantages, which are avoided by the use of the tap devised by Göckel.[1] This is a ridged horizontal tap, sealed by mercury; Lunge states that it is in every way satisfactory and generally applicable.

The pressure tube, C, is now made in the form shown in Fig. 49, which saves a great deal of mercury.

If moist gases are to be measured in the measuring tube, a small drop of water must be introduced into the reduction tube; if dry gases are to be measured, *e.g.*, nitric oxide generated over sulphuric acid in the ordinary nitrometer, a drop of concentrated sulphuric acid is introduced into the reduction tube, but never in sufficient amount to more than cover the top of the mercury meniscus. The gases must be measured either quite dry or saturated with moisture.

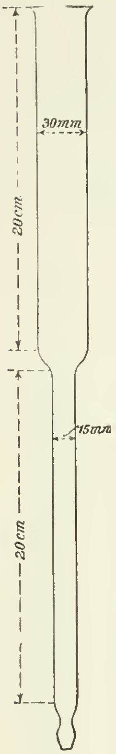

Fig 49.

Formula for dry gases $$V_1 = V_0 \frac{(273+t)760}{273 \times B}$$

Formula for moist gases $$V_1 = V_0 \frac{(273+t)760}{273(B-f)}$$

Where V_1 = Volume of gas required.
V_0 = Normal volume of gas.
t = Observed temperature.
B = Observed barometric pressure.
f = Tension of water-vapour at observed temperature.

To adjust the reduction tube, the temperature is observed by means of a thermometer suspended by the side of the tube, and the barometric pressure read. The volume V_1 which 100 c.c. of gas at normal temperature and pressure V_0 will occupy at the observed temperature and pressure, either dry or moist, is then calculated, either by means of the

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[1] *Z. angew. Chem.*, 1900, **13**, 961 and 1238. This tap is made by Alt, Eberhard, & Jaeger, Ilmenau, Thuringia.

above formulæ or from the Tables VI. to VIII. appended to this volume. The pressure tube is then adjusted, so that the mercury in the reduction tube is at the calculated graduation, and the tap closed. The instrument is then ready for use.

Dry gases can, if desired, be measured with a wet reduction tube, or *vice versa.* In the former case the temperature is observed, the corresponding vapour-tension f in mm. found from Table VIII., and the mercury in the measuring tube placed f mm. higher than in the reduction tube, after the volume in the latter has been adjusted to 100 c.c. This is facilitated by using measuring tubes in which each c.c. of the graduation corresponds almost exactly with 10 mm. length, as the use of a measuring scale is thereby avoided. When a dry reduction tube is used for moist gases, the mercury in the measuring tube must be placed f mm. lower than in the reduction tube, in which the volume has been adjusted to 100 c.c.

An alternative plan for comparing dry gases with a moist reduction tube is to moisten the gas in the measuring tube by drawing in a drop of water; this is preferably done before the gas is collected, but it can also be done afterwards with careful manipulation; for the reverse comparison a drop of concentrated sulphuric acid is used. In neither case must so much liquid be added that it more than covers the top of the mercury meniscus.

The three tubes, A, B, C (Fig. 48), are connected with the T-piece D by very thick-walled rubber tubing of 13·5 mm. external and 4·5 mm. internal diameter. Thick tubing of this character withstands the pressure of the mercury without being distended and does not need binding with wire, especially if the ends of the tubes are enlarged a little; it is easily drawn over tubes of 10 mm. or greater diameter. All three tubes are held in strong clamps, so that they may be moved vertically with friction, but do not drop down by their own weight. If desired, A and B may be fitted with water-jackets, in which case the upper part of B must be cylindrical (as in B, Fig. 52, p. 144), and larger clamps must be used. This addition is quite unnecessary for technical analysis, as the two tubes are placed close together and will only be at different temperatures in case of careless manipulation; also the fairly large mass of mercury greatly assists the equalisation of all temperature differences.

When any gas-analytical or gas-volumetric operation has been carried out in A, the volume of gas is not read in the ordinary manner, after adjusting the mercury in A and C to equal levels. This adjustment is only made as a preliminary step when an auxiliary generating bottle is used, as in decompositions by sodium hypobromite or hydrogen peroxide, or in carbon dioxide determinations, etc.; in these cases the mercury levels in A and C must first be equalised, in order to bring the gas in A to the ordinary atmospheric pressure. The tap of A is then closed, without reading off the volume of contained gas. If the gas has been generated in A itself, or has been transferred from another vessel, this adjustment is of course unnecessary. Before actually reading the volume of gas in A, the three tubes are so adjusted that the mercury in B stands at the 100 c.c. graduation and the levels in A and B are the same. The gas volumes in A and B then correspond to such temperature and pressure that their volumes are equal to those which they would occupy, when dry, at 0° and 760 mm. pressure, since this condition has been ensured once for all in the case of B, and the gas in A is at the same temperature and the same pressure.

The required adjustment is most quickly and easily carried out in the following manner. The tube A is fixed in its clamp whilst B and C are raised, C to such an extent that the mercury in B rises to the graduation 100 c.c.; B and C are then lowered simultaneously, so that the difference of level of the mercury in the two tubes is maintained, until the mercury stands at equal levels in A and B, in the latter still at the 100 c.c. graduation. The adjustment will usually be found to be not quite exact, and a slight movement of B will probably be necessary to complete it, but this double adjustment only requires a few seconds longer than the ordinary adjustment of the pressure tube of a gas-burette. The equalisation of pressure in A and B can be aided by the usual means, such as making the observation against a horizontal wall-line, a window-frame, a special horizontal rod provided with a spirit-level,[1] or in any other manner.

The simultaneous movement of two tubes filled with mercury, as described above, is rather difficult if strong spring clamps are used, and these, moreover, wear out in time. This difficulty is overcome by the use of the forked clamp shown in Figs. 50 and 51.

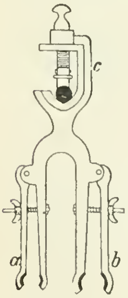

Fig. 50.

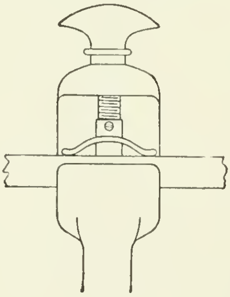

Fig. 51.

This consists of two cork-lined clamps supported by a cast-iron fork. The smaller clamp *a* holds the reduction tube (below the 100 c.c. graduation), and the larger, *b*, the pressure tube. The fork is fastened to the stand by means of an ordinary boss *c*, shown on a larger scale in Fig. 51, which may be strengthened by a spring.[2] By this means the reduction and pressure tubes are held in a common clamp, and can be moved together. After the gas-analytical operation is finished, the adjustment is made by first bringing the reduction and pressure tubes to the approximate level of

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[1] *Cf.* Lunge, *Ber.*, 89, **24**, 3948.

[2] These clamps are made by Desaga, Heidelberg, and other firms.

the mercury in the measuring tube. The pressure tube is then moved in its clamp *b*, until the mercury in the reduction tube stands exactly at the 100 c.c. graduation. The forked clamp is then moved as a whole, by means of the boss *c*, until the mercury levels in the reduction and measuring tubes are equal. The whole adjustment only takes a few seconds, and is much easier than when separately movable clamps are used.

In cases where, in addition to the mercury, another liquid is introduced into the measuring tube, the pressure which it exerts must be taken into account. Thus, in nitrogen determinations by Dumas' method, a mark is made below the 100 c.c. graduation of the reduction tube, corresponding to $\frac{1}{10}$ of the height of the potassium hydroxide solution in the measuring tube, the specific gravity of which may be taken as 1·36, *i.e.*, $\frac{1}{10}$ of that of mercury. In reading off the volume of nitrogen the mercury in the reduction tube is brought to the 100 c.c. graduation, and that in the measuring tube to the level of the special mark below, whereby the height of the potassium hydroxide solution is allowed for.

It is obvious, from the above, that by the use of the gas-volumeter all thermometric and barometric readings, and also all reductions by calculation or by special tables, are avoided; the volume of gas is read off directly under conditions corresponding to the normal pressure and temperature. As already stated (p. 140), the reduction tube must be arranged for dry or moist gas according to the character of the gas-analytical operation.

The measuring tube may be of any of the forms described on pp. 133 to 136. For evident reasons it is, however, not so simple and easy to shake the mercury and sulphuric acid in the tube itself, when a reduction tube is used, and a special danger is that the gas may inadvertently get into the reduction tube. The gas-volumeter is accordingly more applicable for work in which a separate decomposition bottle is used, and for nitrometric analyses, in which the gas is generated in an ungraduated vessel, and then transferred to the volumeter for measurement.

This arrangement of apparatus is shown in Fig. 52. A, B, and C represent the volumeter, as in Fig. 48, p. 139; E is the reaction vessel, and has a capacity of about 100 c.c. when used for the analysis of nitrous vitriol, and of about 200 c.c. for the analysis of saltpetre, dynamite, nitrocellulose, etc.; it is provided with a tap, a beaker *c*, and pressure tube F, arranged as in the ordinary nitrometer. E is best supported by a ring and F by a clamp; E can, of course, be replaced by a Hempel burette or other similar apparatus.

To carry out a determination, F is first raised until the mercury reaches the end of the capillary *a*, which is then closed with a ground-glass or rubber cap *b*, to prevent the escape of mercury on shaking, and the tap of E also closed. The nitrous vitriol or other material is introduced, as usual, through the beaker *c*, the reaction induced by shaking, and the whole allowed to stand until it has acquired the atmospheric temperature. E and A are then brought to the same height, as shown in the figure, and the mercury in the measuring tube of the volumeter A driven over to the end of the thick rubber tube attached to the capillary *d*. The cap *b* is then removed, the capillary *a* slipped into the rubber connecting tube until glass touches glass, F raised and C lowered, the two connecting taps opened, and the gas syphoned from E into A. The tap on A is closed as soon as the acid from E reaches the bottom of the capillary tube *e*. The levels in A and B are then adjusted, and the mercury in B brought to the 100 c.c. graduation, as described above. This method of transferring the gas is advantageous, not only because the pressure due to the sulphuric acid has not to be allowed for, but also because the unavoidable dirtying of the apparatus is confined to the reaction vessel E, which is easily cleaned. Care should be taken that the bores of the capillaries *a* and *d* are not enlarged at the ends, but, if anything, slightly narrowed, so that no bubbles of gas adhere on connecting up. A single-bore tap suffices for the volumeter, and the attached beaker can be dispensed with, as shown in Fig. 52, and this applies also to the use of the apparatus in conjunction with an auxiliary generating bottle, or with a gas-burette. The measuring tube A may be either cylindrical, and of 50 or 100 c.c. capacity, or a bulb-tube graduated from 100 to 140 c.c., etc., according to the special purpose of the apparatus. For general work the form of measuring tube shown in Fig. 46 (p. 136),

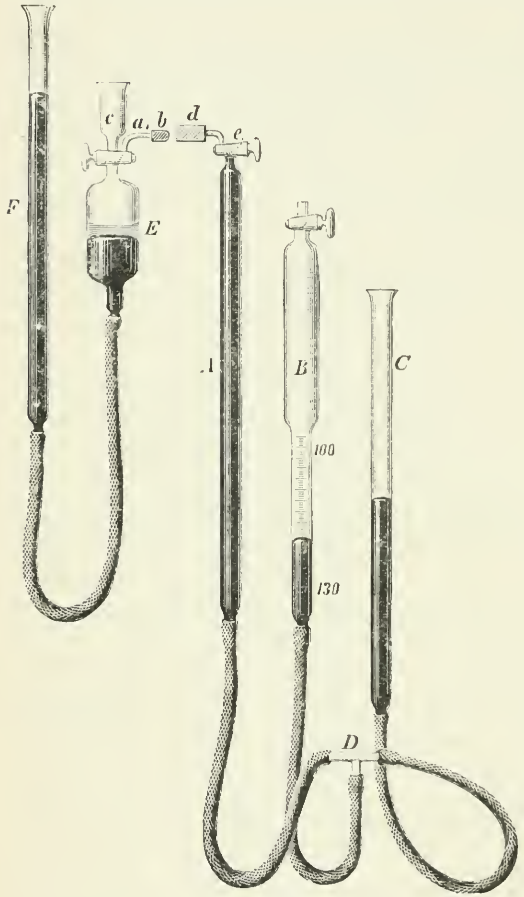

Fig. 52.

with a central bulb, and graduations above and below, is to be recommended.

By using several reaction vessels, many more determinations can be carried out, than with the ordinary nitrometer, in the same time. The contents of the reaction vessels are allowed to cool, after shaking, until the evolved gas is ready for measurement, a new determination started in a second vessel, and so on. In analysing explosives, the funnel of the reaction vessel is connected with the sulphuric acid trap described on p. 136, and shown in Fig. 44.

A modification of the Lunge gas-volumeter, in which all the connections are made of glass, has been described by Gruskiewicz.[1]

Lunge[2] has devised a mechanical stand, which is extremely convenient for manipulating the gas-volumeter, which is described below (p. 154 *et seq.*); it is used by Lunge and Marchlewski with their apparatus for the determination of carbon dioxide and of carbon, and is applicable to all other forms of the nitrometer.

Special forms of the gas-volumeter have been designed by Lunge,[3] for the determination of nitrogen in elementary organic analysis, and by Lunge and Neuberg[4] for the determination of vapour densities.

When the gas-volumeter is in daily use for a specific determination, the graduations on the measuring tube may be made to correspond with definite weights in mg. of the constituent determined, or to percentages, when a definite weight of initial material is taken for analysis. Such graduations may either replace the divisions into c.c., or may be placed alongside them. For nitrogen determinations by Dumas' method, intervals of 0·7997 c.c. are marked off and divided into tenths. As 1 c.c. of nitrogen under normal conditions weighs 1·2505 g., each graduation corresponds to 1 mg. of nitrogen, and the weight of the gas can thus be read directly, as soon as the tube has cooled, after the combustion. For the azometric determination of ammoniacal nitrogen with sodium hypobromite, either the same graduation can be employed, or divisions of 0·658 c.c. = 1 mg. NH_3, since 1 c.c. of nitrogen under normal conditions corresponds to 1·520 mg. NH_3. If, for instance, 0·2 g. of ammonium salt are used, then each such division represents, in the former case, 0·5 per cent. N, and in the latter, 0·5 per cent. NH_3.

For the determination of calcium carbonate in bone, charcoal, marl, and the like, that is for use as a calcimeter, each c.c. CO_2 under normal conditions corresponds to 1·9766 mg. CO_2, or 4·497 mg. $CaCO_3$. If, therefore, a calcimeter is to indicate 1 mg. of $CaCO_3$ for each graduation, these must correspond to 0·222 c.c., and if 0·5 g. substance is used for analysis, then each division will indicate 0·2 per cent.

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[1] *Z. anal. Chem.*, 1904, **43**, 85; *Chem. Centr.*, 1904, I., 1167.

[2] *Z. angew. Chem.*, 1892, **5** 678.

[3] *Ber.*, 1890, **23**, 446.

[4] *Ibid.*, 1891, **24**, 729.

$CaCO_3$. The absorption of carbon dioxide by the generating liquid must, of course, be taken into account, unless it is excluded by using the form of generating apparatus shown in Fig. 53, p. 150.

Such special graduation of the measuring tube is unnecessary, if the quantities given in the following table are used for analysis; an ordinary measuring tube, divided into $\frac{1}{10}$ c.c., can then be employed.

Table for the Conversion of Volumes of Gas, obtained in the Gas-Volumeter, into Weights of Active Constituents.

1	2	3	4	5
Substance Analysed.	Active Constituent.	Method of Analysis.	Gas Evolved.	1 c.c. Gas = Active Constituent in mg.
Organic substances	Nitrogen	Dumas' method	N_2	1·2505
Ammonium salts	Do.	With sodium hypobromite	N_2	1·2818[1]
Do.	Ammonia	Do.	N_2	1·5582[1]
Urine	Urea	Do.	N_2	2·956[1]
Bone-charcoal, marl, etc.	Carbon dioxide	Decomposition by HCl	CO_2	1·976
Do.	Calcium carbonate	Do.	CO_2	4·497
Pyrolusite	Manganese dioxide	With H_2O_2	O_2	3·885
Bleaching powder	Chlorine	Do.	O_2	1·6095
Potassium permanganate	Oxygen	Do.	O_2	0·7146
Chili saltpetre	Sodium nitrate	In nitrometer	NO	3·7986
Nitrous vitriol	N_2O_3	Do.	NO	1·6975
Do.	HNO_3	Do.	NO	2·8144
Do.	Nitric acid of sp. gr. 1·33.	Do.	NO	5·3771
Do.	Sodium nitrate	Do.	NO	3·7986
Nitroglycerine, dynamite, etc.	Trinitroglycerine	Do.	NO	3·358
Do.	Nitrogen	Do.	NO	0·6257
Nitrocellulose, pyroxylin	Do.	Do.	NO	0·6257

[1] These values are corrected for the "nitrogen absorption"; 2·5 per cent. in the case of ammonium salts, and 9 per cent. in the case of urea. (*Cf.* p. 131.)

The table comprises a number of substances, specified in the first column, which are frequently examined by gas-volumetric methods. The second column gives the "active constituent" of the substance analysed; the third column, the analytical method employed; the fourth, the nature of the evolved gas; the fifth, the weight of "active constituent" in mg. corresponding to 1 c.c. of gas at 0° and 760 mm. pressure. If one hundred times the quantity of substance given in column 5 is taken, then the number of c.c. of gas obtained is numerically equal to the percentage of the active constituent. In some cases it is necessary to use a larger quantity of substance, and then 1 c.c. of gas represents, of course, a correspondingly smaller percentage.

The data given in this table are based on the observed densities of the gases[1] concerned, not on the values calculated from the molecular weights, which do not take into account the deviations from Boyle's law.

When the gas-volumeter is used as an azotometer, an addition of 2·5 per cent. of the volume of gas obtained must be added, to allow for the incompleteness of the reaction, the so-called "nitrogen absorption" (*cf.* p. 131). With this correction, 1 c.c. of nitrogen under normal conditions corresponds to 1·2818 mg. ammoniacal nitrogen or 1·5582 mg. ammonia, so that 0·1282 g. or 0·1558 g. of ammonium salt must be taken for analysis, if 1 c.c. of gas is to correspond to 1 per cent. of N or of NH_3 respectively.

Japp[2] has shown, that by suitably adjusting the position of the reduction tube, the volume of gas in the measuring tube may be made to indicate the weight of active substance present, without further calculation and without special graduation. As an example, suppose that a reduction tube is used, the normal volume of which is 25 c.c., that is, the gaseous contents occupy this volume at 0° and 760 mm. pressure; the weight of 1 c.c. of nitrogen under these conditions is 0·0012505 g., and of the 25 c.c. $0·0012505 \times 25 = 0·03126$ g. If the reduction tube is adjusted so that the volume of contained gas is 31·3 c.c., each c.c. of gas in the measuring tube will then correspond to 1 mg. of nitrogen.

According to Lunge,[3] 25 c.c. is too small a normal volume to adopt for accurate work, and it is preferable to use an ordinary reduction tube, or one of 90 to 150 c.c. capacity, which is adjusted to contain 100 c.c. under normal conditions. To convert the volume of gas into its equivalent in mg., the mercury in the reduction tube is adjusted so that the volume is equal to 100 c.c., multiplied by the weight of gas per litre, thus :—

For atmospheric air . . .	129·3 c.c.
„ oxygen	142·9 c.c.
„ nitrogen	125·05 c.c.
„ nitric oxide	134·02 c.c.

The corresponding figure for carbon dioxide being 197·66 c.c., which would extend beyond the graduations, the reduction tube is adjusted to 98·8 c.c. in this case, so that each c.c. in the measuring tube corresponds to 2 mg. of gas. This principle may be extended so that the volumes of gas found correspond, not to weights of gas, but to weights of the active constituent of the substance analysed. Thus, in determining the

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[1] The densities are taken from the *Physikalisch-chemische Tabellen* of Llandolt-Börnstein, 3rd edition, 1905.

[2] *J. Chem. Soc.*, 1891, **59**, 894; *cf.* also Lunge, *Ber.*, 1891, **24**, 1656 and 3491.

[3] *Ber.*, 1892, **25**, 3162.

amount of active chlorine in bleaching powder, by means of hydrogen peroxide, oxygen is obtained instead of chlorine, volume for volume; by adjusting the reduction tube to $\frac{1}{3}$ of the weight of a litre of chlorine, that is, to 107·3 c.c., each c.c. of gas in the measuring tube corresponds to 3 mg. Cl. In order to read off weights of $CaCO_3$ instead of CO_2, the volume in the reduction tube is adjusted to $\frac{197 \cdot 6 \times 100}{44 \times 4} = 112 \cdot 3$ c.c.; 1 c.c. of CO_2 in the measuring tube then represents 4 mg. $CaCO_3$.

Japp's proposal, even with the above extensions, seldom offers, however, any advantage over the method of working described above (p. 145 *et seq.*), and set out in the table, according to which the quantity of substance taken for analysis is such, that on adjusting the reduction tube to 100 c.c., percentages may be read directly in the measuring tube.

Other forms of apparatus for measuring gases, without the necessity for barometric and thermometric readings, have since been constructed by Hempel,[1] Bleier,[2] Bodländer,[3] and others.

The barothermoscope devised by F. Salomon[4] is provided with a scale on which the volume, corresponding to the temperature and pressure of the surrounding gas, can be read off directly. The instrument is most ingenious, and is based on the new thermometric system proposed by Salomon; it is, however, rather troublesome to adjust and difficult to transport, and has accordingly not been adopted for practical work.

A. Wohl[5] has described an apparatus for measuring the volume of gases by determining the pressure, a vessel of constant volume being employed for the purpose. Wohl and Poppenberg[6] have extended this method, especially to the determination of nitrogen in nitrates and nitric esters such as gun-cotton, etc.

Apparatus for the determination of Carbon Dioxide.

This section is restricted to a description of the methods for the gas-volumetric determination of carbon dioxide generated from solid and liquid substances. The methods for the determination of carbon dioxide in gaseous mixtures are dealt with under "Technical Gas Analysis"; the various forms of apparatus for the determination of carbon dioxide, by loss of weight, in calcimeters, in which the gas is expelled by means of a stronger acid, are also omitted, as they never give very accurate results.

Both the azotometer (p. 125) and the nitrometer (p. 132) may be used for the gas-volumetric determination of carbon dioxide, but they

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[1] *Z. angew. Chem.*, 1894, **7**, 22.

[2] *Ber.*, 1897, **30**, 2733; 1898, **31**, 236.

[3] *Z. angew. Chem.*, 1895, **8**, 49.

[4] *Ibid.*, 1893, **6**, 376; 1894, **7**, 686.

[5] *Ber.*, 1902, **35**, 3493; 1903, **36**, 674.

[6] *Ibid.*, 1903, **36**, 676.

involve difficulties, on account of the solubility of the gas in the liquid present in the decomposition vessel and in the water over which it is collected, in the case of the azotometer.

Many suggestions have been made to overcome these difficulties, either by the use of a special confining liquid, over which the gas is collected, as in the apparatus patented by Baur,[1] which is merely a simplified and less effective form of azotometer, or by the use of correction tables, as in Scheibler's apparatus, which is used chiefly in sugar works, in those of Dietrich and of Michaëlis, which are largely used in cement works, and in those of Rumpf, Thörner, Fuchs, and many others.

Satisfactory results were first obtained with the apparatus devised by Pettersson,[2] in which the carbon dioxide is finally displaced by hydrogen, generated from iron or from aluminium wire, the gases collected over mercury, and the carbon dioxide absorbed in an Orsat apparatus. The expulsion of the carbon dioxide is, however, only complete after three or four repetitions of the operation, and the volume of gas obtained must be corrected to normal temperature and pressure in the usual way; the method is therefore unsuitable for technical laboratories.

The successful solution of the above difficulties has been effected by Lunge and Marchlewski.[3] Their method resembles that of Pettersson, but the gas is completely expelled by a single boiling, and no readings of the thermometer and barometer or calculations are required, as the apparatus is so arranged that weights or percentages may be read off directly. Although the apparatus appears, at first sight, as complicated as many others devised for the same purpose, its manipulation is very simple; a determination can be performed in a few minutes, with greater exactitude than can be obtained by any other process, including the titrimetric and the volumetric methods, as it avoids certain sources of error which are inherent to the latter.

The apparatus is shown in $\frac{1}{6}$ the actual size in Fig. 53; Fig. 54 shows an improved form of the generating flask on $\frac{1}{2}$ scale. For solid substances, a flask of 30 c.c. capacity is used; for solutions and for other special purposes, such as the determination of carbon in iron,[4] a large flask is employed, to which a small reflux condenser is attached.

The flask A is closed by a good soft rubber stopper, in which a dropping-funnel *a* and a capillary tube *bd*, bent at right angles, are fixed. The latter is 30-35 cm. long, and is connected with

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[1] *Z. anal. Chem.*, 1884, **23**, 371.

[2] *Ber.*, 1890, **23**, 1402.

[3] *Z. angew. Chem.*, 1891, **4**, 229; 1893, **6**, 395. *J. Soc. Chem. Ind.*, 1891, **10**, 658.

[4] Cf. *Stahl und Eisen*, 1891, **11**, 666; 1893, **13**, 655; 1894, **14**, 624; also, *Z. angew. Chem.*, 1891, **4**, 412. (Determination of carbon in iron and steel, and of carbon dioxide in aqueous solutions.)

the lateral capillary *e* of a gas-volumeter B. The measuring tube of the volumeter ends in a bulb of about 100 c.c. capacity, below which the tube is graduated in $\frac{1}{10}$ c.c. for another 50-60 c.c. The form of tube, described below, in connection with the "Universal Gas-volumeter" may also be used, but it is not so suitable.

The glass tap *f* has two oblique passages (*cf.* p. 134), one of which connects through the tube *e* to *d*, and the other through the tube *g*, and the two-way tap *h* to the "absorption vessel" E, which is rather more than half-filled with a solution of 1 part of sodium hydroxide in 3 parts of water; its outer limb is surmounted by a tube *i*, filled with soda-lime. B communicates below, by means of a T-piece and thick rubber tubing, with the reduction tube C (p. 139), which is graduated below the bulb between 100-130 c.c., and with the pressure tube D, which also serves as a pump; the two tubes are held by the forked clamp *l* (p. 142), so that they can be moved either separately or simultaneously. B, C, and D are filled with mercury.

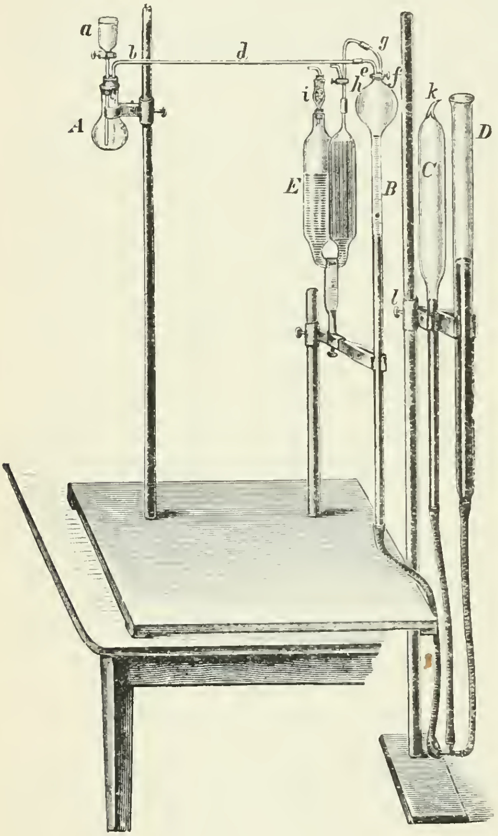

Fig. 53.

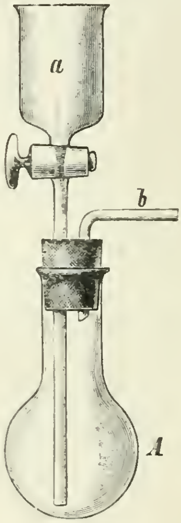

Fig. 54.

Instead of the reduction tube ending in a capillary, as shown in the figure, it is better to use one fitted with a Göckel's mercury-tap (p. 140). The adjustment of the reduction tube is made for moist air as described above (p. 140). If no barometer is available for this purpose, the apparatus itself may be used to determine the atmospheric pressure, as follows. The tap on C is momentarily closed, all air expelled from B by raising D, the tap *f* closed, and D lowered by about 0·5 m. to make sure that no air leaks in through *f*; D is then lowered for another 0·3 m. approximately, so that the mercury just leaves the tap *f* and the vertical distance between the mercury levels in B and D, which represents the barometric pressure, measured.

It is advisable to bind all the rubber tubes to the glass with fine wire, with the exception of the connection between *d* and *e*, which has to be separated for each determination; the apparatus should always be tested before use, to make sure that it is air-tight.

To carry out a determination, the flask A is cleaned, care being taken to remove all traces of acid, and a weighed quantity of the substance for analysis introduced, together with about 0·08 g. of finest aluminium wire. The best plan is to weigh out 0·08 g. of the stock of aluminium wire, measure its length, cut off a number of similar pieces and make each into a little roll, for use in each determination; this amount of aluminium should generate about 100 c.c. of hydrogen. After the introduction of the substance and of the aluminium, the stopper is replaced, *d* connected with *e*, and the air evacuated from A by lowering D as far as possible and then expelling the air, drawn into B, by raising D until the mercury reaches the tap *f*; this operation is repeated two or three times. A few c.c. of pure hydrochloric acid, diluted with three times its volume of boiled distilled water, are then added through *a*, and the flask A warmed gently, with a spirit-lamp, for about two minutes; a further quantity of dilute acid is then added, the flask again warmed for two minutes, and this operation repeated. In this way the carbon dioxide is liberated and the hydrogen generated from the aluminium at the same time; all the carbon dioxide dissolved in the liquid is expelled by the hydrogen, assisted by the diminished pressure in the apparatus. Meanwhile D is placed so that the contained mercury is at a lower level than in B. If the evolution of gas becomes too vigorous, the heating is discontinued. When all the aluminium is dissolved and the liquid is quite clear, dilute acid is added through *a* until the flask A and the tubes *b* and *d* are quite full, almost as far as the tap *f*; after closing *f* the apparatus is allowed to stand for ten minutes for the temperature to become equalised. Meanwhile A and *d* may be removed, cleaned, and the substance for the next determination weighed out.

To prepare the pipette E for the absorption of the carbon dioxide, air is blown in through *i* until the sodium hydroxide solution flows out from the outer tube, leading from the tap *h*, which is then closed. C and D are then adjusted until the mercury in C is at the 100 c.c. graduation and also at the same height as in B. The volume of gas in B is read off, and then transferred to E, three times in succession, to absorb the carbon dioxide, after turning the tap *h* so that E and *g* communicate, and opening the tap *f*. The solution in E is finally syphoned back to the tap *h*, C and D adjusted as before, and the volume of gas in B again read off. If large quantities of carbon dioxide have been absorbed, the apparatus should again be allowed to stand for a few minutes so that the temperature may become equalised.

Any small quantity of water which may get over into B, on heating A, may be disregarded, the volume of gas in B being read from the top of the mercury meniscus, both before and after the absorption of the carbon dioxide.

The difference in the readings before and after the absorption of the carbon dioxide represents the volume of the gas at 0° C. and 760 mm. pressure. If it amounts to n c.c. it corresponds to $n \times 1{\cdot}976$ mg. CO_2, or $n \times 4{\cdot}497$ mg. $CaCO_3$. If p g. of substance were used for analysis, then the percentage of CO_2 is $\frac{n \times 0{\cdot}1976}{p}$, and the percentage of $CaCO_3$ $\frac{n \times 0{\cdot}4497}{p}$. This calculation may be avoided by the following method, which enables percentages to be read off directly.

Suitable amounts of the material under examination are weighed out; if percentages of CO_2 are required, the following amounts are taken:—

For substances which contain much CO_2	0·1976 g.;	1 c c = 1 per cent. CO_2
For substances which contain less CO_2	0·3952 g.;	1 c.c. = 0·5 per cent. CO_2
For substances which contain little CO_2	1·976 g.;	1 c.c. = 0·1 per cent. CO_2

If percentages of $CaCO_3$ are required, the following amounts are taken:—

For pure limestone	0·1799 g.;	1 c.c. = 2·5 per cent. $CaCO_3$
For marls rich in calcium carbonate .	0·2248 g.;	1 c.c. = 2·0 per cent. $CaCO_3$
For marls poor in calcium carbonate .	0·4497 g.;	1 c.c. = 1·0 per cent. $CaCO_3$
Substances containing very little calcium carbonate, cements, etc. .	2·248 g.;	1 c.c. = 0·2 per cent. $CaCO_3$

Examples.

A. *Marl rich in calcium carbonate.* Weight of substance: 0·2248 g. First reading: 145·3 c.c. Second reading after absorption of CO_2: 103·7 c.c. Difference: 41·6 c.c. $41{\cdot}6 \times 2 = 83{\cdot}2$ per cent. $CaCO_3$.

B. *Portland cement.* Weight of substance: 2·248 g. First reading: 116·9 c.c. Second reading: 110·4 c.c. Difference: 6·5 c.c. $6{\cdot}5 \times 0{\cdot}2 = 1{\cdot}3$ per cent. $CaCO_3$.

Or:—Weight of substance: 1·976 g. First reading: 116·1 c.c.

Second reading: 110·4 c.c. Difference: 5·7 c.c. 5·7 × 0·1 = 0·57 per cent. CO_2.

The above method for the estimation of carbon dioxide has recently been considerably simplified by Lunge and Rittener,[1] and rendered applicable to the determination of this gas in the presence of chlorine or of sulphuretted hydrogen. The decomposition of the salt is conducted exactly as in the Lunge-Marchlewski method, and a similar flask is used for this purpose, but the volumeter and absorption pipette are replaced by an ordinary cylindrical Bunté burette. A saturated brine solution is used, instead of mercury, as the confining liquid. The method and apparatus is described in detail in connection with the determination of chlorine and carbon dioxide (p. 514, Fig. 146). To carry out a determination, the decomposition bottle is first connected by means of the capillary tube (*b d*, Fig. 53) to the capillary exit-tube of the burette, and the whole exhausted by attaching an ordinary pump to the lower tap of the burette; sufficient exhaustion is obtained in two to three minutes, and the burette tap is then closed and connected with the pressure bottle in the usual way. As a check on any possible leakage at this tap, a little of the brine solution is introduced from the pressure bottle, so as to just fill the capillary portion of the bottom of the nitrometer, and the tap again closed. After the completion of the decomposition, the burette is disconnected, allowed to stand for twenty to twenty-five minutes, and the volume of gas read, after adjusting the pressure, and corrected for temperature and pressure. The contained carbon dioxide is then absorbed by introducing a solution of sodium hydroxide (1 : 2) into the burette, through the attached funnel; the contents of the burette are well shaken, to promote the absorption of the carbon dioxide, and further successive portions of sodium hydroxide are introduced until there is no further decrease in volume. The final reading is then taken and corrected for temperature and pressure as usual. The difference between the two readings, before and after the absorption by sodium hydroxide, gives the volume of carbon dioxide obtained. In correcting the volume of gas, the vapour tension of the salt solution may be taken as 80 per cent. of that of pure water. The solubility of carbon dioxide in the brine solution is negligible, as the gas is only in contact with a small surface of the solution and is not shaken up with it. Results obtained by the authors with pure sodium carbonate, with cement and with marl, agree well with those got by the Lunge-Marchlewski method. The application of the method to the determination of carbon dioxide in presence of sulphuretted hydrogen is described on p. 439, and in presence of chlorine on p. 514.

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[1] *Z. angew. Chem.*, 1906, **19**, 1849.

The Universal Gas-Volumeter.[1]

The manipulation of the Lunge-Marchlewski apparatus is greatly facilitated by the use of the mechanical stand mentioned above

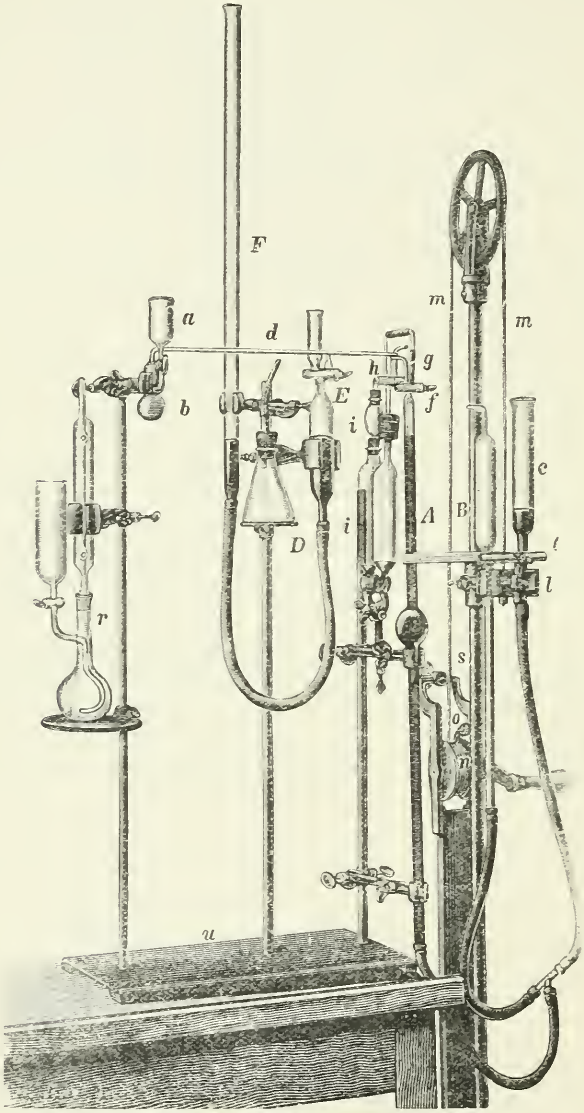

Fig. 55.

(p. 149). This is shown apart from its base in Fig. 55, which

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[1] This apparatus with all necessary fittings is supplied by C. Desaga, Heidelberg, and by A. Jöge, Zurich.

represents the Universal Gas-Volumeter, as arranged by Lunge for all gas-volumetric work. A is the measuring tube, B the reduction tube, and C the pressure tube, as in the ordinary gas-volumeter. E is the reaction or shaking vessel for the analysis of saltpetre, dynamite, etc. (p. 144), with pressure tube F, and auxiliary bottle D (p. 137). The parts *a* to *i* serve for determinations of carbon dioxide, as in Fig. 53. The mechanical stand permits the rough adjustment of the forked clamp *l* by means of the steel wire rope *m*; this is wound on to the drum *n*, which is provided with a spiral groove, and with a brake *o* acting on a cogged wheel, by means of the handle *p*. Five or six turns of the handle suffice to move the forked clamp from the highest to the lowest position (*e.g.*, for evacuating). The brake *o* works automatically when the clamp is being raised; whilst lowering, it is thrown out of action by means of the small clutch shown in the figure. The exact adjustment of the clamp *l* is effected by the screw *s*, connected with the support of the drum; this screw acts as a fine adjustment, by pressing the wire rope forwards out of its direct position, thus increasing the tension on the wire.

Both the reduction tube B and the pressure tube C can, of course, be moved independently, as is always necessary for the final adjustment; much relative adjustment of these two tubes is not usually required, as the volume of air in the reduction tube is generally kept in the neighbourhood of 100 c.c.

A straight-edge (p. 142) with spirit-level *t*, and supported by an extension of the clamp *l*, may be used for the final adjustment;[1] it should reach across to the measuring tube A.

The measuring tube A is suitable for all classes of analyses. It has a capacity of about 140 c.c. (150 c.c. would be preferable, were it not for the added length), and is graduated from the top, in $\frac{1}{10}$ c.c., from 0 to 30 c.c.; this portion of the tube is followed by a bulb, below which the graduation is continued from 100 to 140 c.c. The measurement of both small and large quantities of gas is thus provided for. The tube can be moved in its two clamps, but this is not usually necessary, as all adjustments are effected by means of the clamp *l*.

General Remarks on Measuring Vessels for Gases.

As emphasised on p. 44, it is essential that accurate apparatus should be used for measuring gases; it should, therefore, be either calibrated, or controlled and stamped by a recognised authority. In the case of ordinary gas analyses, the main requirement is that the volumes marked as c.c. should be actually equal to one another, but in the case of gas-volumetric work, it is important that the graduations

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[1] Cf. *Ber.*, 1891, **24**, 3948.

should correspond to actual c.c., as the weight of gas is deduced from its volume. In calibrating the measuring vessels the following points must be observed:—1. The adhesion of the confining liquid used; in the case of mercury this is zero, but it must be allowed for with water, aqueous solutions, petroleum, etc. 2. The meniscus correction, which varies, of course, with the nature of the liquid employed, and which must be specially taken into account when the calibration by weighing water or mercury is done in an inverted position to that in which the vessel is subsequently used. Göckel[1] is quite justified in contending that the graduations of gas measuring vessels should be clearly stated, *e.g.*, "Corr. for H_2O" or "Corr. for Hg."

I. DETERMINATION OF SPECIFIC GRAVITY

The determination of the specific gravity of liquids plays an extremely important part in chemical technology. It is almost exclusively measured by means of hydrometers; pyknometers, the Westphal balance, and other well-known forms of apparatus for the determination of specific gravity, are only used occasionally. It is, however, very desirable that a works' laboratory should possess some instrument with which to control the readings of hydrometers, as the latter, especially the cheaper kinds, are very often inaccurate.

A very reliable method of control consists in determining the specific gravity of a suitable liquid, by weighing it in a calibrated litre flask, to within 0·1 g., and then testing it with the hydrometers under examination, using tables for the reduction of their readings to specific gravities (cf. *infra*). The temperature for which the hydrometers are calibrated must, of course, be adhered to. Hydrometers must not be greasy, soiled, or damp, before introduction into the liquid; they must be immersed carefully, and must be read from below, at the height of the meniscus of the liquid, that is, at A_1 A_2 (Fig. 56), and not at B_1 B_2.

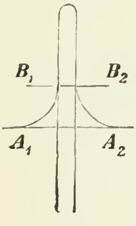

FIG. 56.

Hydrometers which indicate the specific gravity directly are fairly often used for liquids lighter than water, and it would be advantageous if they were used more in other cases, instead of the various scales of Baumé, Beck, etc.; they are practically never used in works for specific gravities above 1·0. Fleischer's "Densimeter," the graduations of which represent multiples of 0·01, and are convertible into actual specific gravities by addition of 1, have unfortunately almost entirely failed to be adopted in practice; on this scale, 7° D = 1·07; 25° = 1·25, etc.

Densimeter degrees are rather large. In the Twaddell hydrometer,

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[1] Cf. *Chem. Zeit.*, 1902, **26**, 159.

which was used in this country long before the introduction of Fleischer's densimeter, and which is still in general use for technical work, the degrees are half of the above value. Each degree corresponds to 0·005 sp. gr., prefixed by unity. Thus, 7° Tw. = 1·035; 20° Tw. = 1·100; 100° Tw. = 1·500 sp. gr., etc. No table is therefore required for the conversion of degrees Twaddell into ordinary specific gravities, and the value of a degree Twaddell is quite definite. It is remarkable that this rational and practical hydrometer, the scale of which is usually distributed over six spindles, should be almost universally used in this country, which is so very conservative and unpractical with regard to weights and measures, whilst the continental nations, which have all adopted the metric system of weights and measures (with the exception of Russia), have not yet adopted a rational hydrometer.

In the United States, the Baumé hydrometer is used, for which a special scale, different to that employed in other countries, has been adopted.

During the last generation, France, Germany, and other continental countries have adopted the Baumé scale almost universally, to the exclusion of others; the advantage thus gained is, however, very limited, as there is no exact and recognised interpretation of the significance of a Baumé degree. The hydrometers were originally graduated by calling the point up to which they sank in pure water 0°, and that up to which they sank in a 10 per cent. salt solution at 17°·5 C., 10° B. The intermediate space was then divided into 10 equal parts, and these "degrees" continued upwards, at equal intervals, so that the scale value of each degree was the same, but in no way corresponded to equal changes in specific gravity. The scale was also affected by the fact that the salt used was seldom pure and dry, so that the specific gravity of a so-called 10 per cent. salt solution varied considerably. Determinations by Gerlach gave the value 1·07311 at 14° R. (17°·5 C.), and from this he calculated a table comparing Baumé degrees with specific gravities.[1] It is doubtful whether hydrometers, according to Gerlach's scale, are made now; their lower degrees do not agree with those ordinarily used, and the higher ones show extraordinary differences. Thus, according to Gerlach's values, 66° B. = sp. gr. 1·8171, which would correspond with a sulphuric acid of 89·5 per cent. H_2SO_4, whereas the real value of 66° B. is 93 per cent. H_2SO_4.

The modern practice is to mark the hydrometers 66° B., at the point to which they sink in "English sulphuric acid" (*i.e.*, sulphuric acid of 93 to 95 per cent. H_2SO_4) at 17°·5 C., and to divide the space between this and 0° into 66 equal parts. But uncertainty is introduced in the definition "English sulphuric acid." Pure acid was certainly never employed, as is proved by the fact that

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[1] *Dingl. polyt. J.*, 1870, **198**, 315.

the specific gravity 1·842, which is usually considered the equivalent of 66° B., is certainly greater than that of pure sulphuric acid at 17°·5 C., even at its point of maximum density (97·5 per cent. H_2SO_4). Apart from this, there is the uncertainty as to the percentage composition of the acid. Accordingly, many and very varying scales of the Baumé hydrometer were placed on the market; a test made by C. F. Chandler (1881) disclosed thirty-four different scales, none of which were correct. About twenty-five years ago, Kolb, in France, tried to remove this confusion by the construction of a "rational" Baumé hydrometer, the scale of which was based on the following perfectly sound physical principle.

If a hydrometer sinks in water to 0°, and in a liquid D, of specific gravity d, to $n°$, then the weight of the volume of displaced liquid is, in each case, equal to the weight (G) of the hydrometer, thus:—

Weight of water displaced by hydrometer = G
Weight of an equal volume of liquid D = d G
Weight of water displaced by n scale divisions = n
Weight of an equal weight of liquid D = nd

As the weights d G and G differ by nd,

$$d\mathrm{G} - \mathrm{G} = nd\,;\ \text{therefore,}\ d = \frac{\mathrm{G}}{\mathrm{G}-n}\ \text{and}\ \mathrm{G} = \frac{nd}{d-1}.$$

If, according to Kolb, 66° B. is taken to correspond to sp. gr. 1·842 at 15° C, then when $n=66$, $d=1{\cdot}842$. This gives $\mathrm{G}=1{\cdot}443$, and

$$d = \frac{144{\cdot}3}{144{\cdot}3-n}.$$

The formulæ in the subjoined table are calculated from the values v, for the specific gravity of a 10 per cent. salt solution.

Temperature in degrees C.	v.	Liquid heavier than Water.	Liquid lighter than Water.
12°·5 C.	1·073596	$d = \frac{145{\cdot}88}{145{\cdot}88-n}$	$d = \frac{145{\cdot}88}{135{\cdot}88+n}$
15°·0 C.	1·073350	$d = \frac{146{\cdot}3}{146{\cdot}3-n}$	$d = \frac{146{\cdot}3}{136{\cdot}3+n}$
17°·5 C.	1·073110	$d = \frac{146{\cdot}78}{146{\cdot}78-n}$	$d = \frac{146{\cdot}78}{136{\cdot}78+n}$

Kolb's hydrometer, though based on an inexact specific gravity for pure sulphuric acid, *i.e.*, 1·842, is more concordant, especially for the higher degrees, than the Gerlach hydrometers, based on the 10 per cent. salt solution. It has not, however, been generally adopted even in

France, but it is used to a considerable extent in Germany. Two other "rational" Baumé scales are in use, namely, that used in Holland, in which $d=\frac{144}{144-n}$, and that adopted in America, in which $d=\frac{145}{145-n}$.

In the following table the specific gravities corresponding to the "Rational," Gerlach and American Baumé scales, are given;[1] the table issued by the German Normal Standards Commission in 1904, for the conversion of specific gravities at $\frac{15^{\circ}}{4}$ into "rational" Baumé degrees is also given.

Comparison of various Baumé Hydrometers, for Heavy Liquids, with Specific Gravities.

Degrees.	Rational Hydrometer. $d=\frac{144\cdot3}{144\cdot3-n}$.	Baumé's Hydrometer according to Gerlach's Scale.	American Scale. $d=\frac{145}{145-n}$.	Degrees.	Rational Hydrometer. $d=\frac{144\cdot3}{144\cdot3-n}$.	Baumé's Hydrometer according to Gerlach's Scale.	American Scale. $d=\frac{145}{145-n}$.
1	1·007	1·0068	1·005	34	1·308	1·3015	1·309
2	1·014	1·0138	1·011	35	1·320	1·3131	1·317
3	1·022	1·0208	1·023	36	1·332	1·3250	1·334
4	1·029	1·0280	1·029	37	1·345	1·3370	1·342
5	1·037	1·0353	1·036	38	1·357	1·3494	1·359
6	1·045	1·0426	1·043	39	1·370	1·3619	1·368
7	1·052	1·0501	1·050	40	1·383	1·3746	1·386
8	1·060	1·0576	1·057	41	1·397	1·3876	1·395
9	1·067	1·0653	1·064	42	1·410	1·4009	1·413
10	1·075	1·0731	1·071	43	1·424	1·4134	1·422
11	1·083	1·0810	1·086	44	1·438	1·4281	1·441
12	1·091	1·0890	1·093	45	1·453	1·4421	1·451
13	1·100	1·0972	1·100	46	1·468	1·4564	1·470
14	1·108	1·1054	1·107	47	1·483	1·4710	1·480
15	1·116	1·1138	1·114	48	1·498	1·4860	1·500
16	1·125	1·1224	1·122	49	1·514	1·5012	1·510
17	1·134	1·1310	1·136	50	1·530	1·5167	1·531
18	1·142	1·1398	1·143	51	1·540	1·5325	1·541
19	1·152	1·1487	1·150	52	1·563	1·5487	1·561
20	1·162	1·1578	1·158	53	1·580	1·5652	1·573
21	1·171	1·1670	1·172	54	1·597	1·5820	1·594
22	1·180	1·1763	1·179	55	1·615	1·5993	1·616
23	1·190	1·1858	1·186	56	1·634	1·6169	1·627
24	1·200	1·1955	1·201	57	1·652	1·6349	1·650
25	1·210	1·2053	1·208	58	1·671	1·6533	1·661
26	1·220	1·2153	1·216	59	1·691	1·6721	1·683
27	1·231	1·2254	1·231	60	1·711	1·6914	1·705
28	1·241	1·2357	1·238	61	1·732	1·7111	1·727
29	1·252	1·2462	1·254	62	1·753	1·7313	1·747
30	1·263	1·2569	1·262	63	1·774	1·7520	1·767
31	1·274	1·2677	1·269	64	1·796	1·7731	1·793
32	1·285	1·2788	1·285	65	1·819	1·7948	1·814
33	1·297	1·2901	1·293	66	1·842	1·8171	1·835

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[1] The figures for the American Baumé scale are taken from the *Chemical Trade Journal*, 1887, 2, 183.

Table for the Conversion of Specific Gravities, at $\frac{15^{\circ}}{4^{\circ}}$, into "Rational" Baumé degrees.

Sp. gr.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0·99	...	...	...	...	...	...	...	...	...	– 0·018
1·00	0·126	0·270	0·414	0·557	0·700	0·843	0·986	1·128	1·270	1·412
01	1·553	1·694	1·835	1·976	2·117	2·257	2·397	2·536	2·675	2·814
02	2·953	3·091	3·229	3·367	3·505	3·643	3·780	3·917	4·053	4·189
03	4·325	4·461	4·596	4·731	4·866	5·001	5·135	5·269	5·403	5·537
04	5·671	5·804	5·937	6·070	6·202	6·334	6·466	6·598	6·729	6·860
1·05	6·991	7·122	7·252	7·382	7·512	7·642	7·771	7·900	8·029	8·158
06	8·287	8·415	8·543	8·671	8·798	8·925	9·052	9·179	9·306	9·432
07	9·558	9·684	9·809	9·934	10·059	10·184	10·309	10·433	10·557	10·681
08	10·805	10·929	11·052	11·175	11·298	11·421	11·543	11·665	11·787	11·909
09	12·030	12·151	12·272	12·393	12·514	12·634	12·754	12·874	12·994	13·114
1·10	13·233	13·352	13·471	13·590	13·708	13·826	13·944	14·062	14·179	14·296
11	14·413	14·530	14·647	14·764	14·880	14·996	15·112	15·228	15·343	15·458
12	15·573	15·688	15·803	15·917	16·031	16·145	16·259	16·373	16·486	16·599
13	16·712	16·825	16·938	17·050	17·162	17·274	17·386	17·498	17·610	17·721
14	17·832	17·943	18·054	18·164	18·274	18·384	18·494	18·604	18·713	18·822
1·15	18·931	19·040	19·149	19·258	19·366	19·474	19·582	19·690	19·798	19·905
16	20·012	20·119	20·226	20·333	20·439	20·545	20·651	20·757	20·863	20·969
17	21·074	21·179	21·284	21·389	21·494	21·599	21·703	21·807	21·911	22·015
18	22·119	22·222	22·325	22·428	22·531	22·634	22·737	22·839	22·941	23·043
19	23·145	23·247	23·349	23·450	23·551	23·652	23·753	23·854	23·955	24·055
1·20	24·155	24·255	24·355	24·455	24·554	24·653	24·752	24·851	24·950	25·049
21	25·148	25·246	25·344	25·442	25·540	25·638	25·736	25·834	25·931	26·028
22	26·125	27·222	26·319	26·415	26·511	26·607	26·703	26·799	26·895	26·990
23	27·085	27·180	27·275	27·370	27·465	27·560	27·655	27·749	27·843	27·937
24	28·031	28·125	28·219	28·312	28·405	28·498	28·591	28·684	28·777	28·869
1·25	28·961	29·053	29·145	29·237	29·329	29·420	29·512	29·603	29·694	29·785
26	29·876	29·967	30·058	30·149	30·239	30·329	30·419	30·509	30·599	30·688
27	30·777	30·866	30·955	31·044	31·133	31·222	31·311	31·400	31·488	31·576
28	31·664	31·752	31·840	31·928	32·015	32·102	32·189	32·276	32·363	32·450
29	32·537	32·624	32·711	32·797	32·883	32·969	33·055	33·141	33·227	33·312
1·30	33·397	33·482	33·567	33 652	33·737	33·822	33·907	33·991	34·075	34·159
31	34·243	34·327	34·411	34·495	34·579	34·662	34·745	34·828	34·911	34·994
32	35·077	35·160	35·243	35·325	35·407	35·489	35·571	35·653	35·735	35·817
33	35·899	35·981	36·062	36·143	36·224	36·305	36·386	36·467	36·548	36·628
34	36·708	36·788	36·868	36·948	37·028	37·107	37·187	37·267	37·346	37·425
1·35	37·504	37·583	37·662	37 741	37·820	37·898	37·977	38·056	38·134	38·212
36	38·290	38·368	38·446	38·524	38·601	38·678	38·755	38·832	38·909	38·986
37	39·063	39·140	39·217	39·294	39·370	39·446	39·522	39·598	39·674	39·750
38	39·826	39·902	39·978	40·053	40·128	40·203	40·278	40·353	40·428	40·503
39	40·578	40·653	40·727	40·801	40·875	40·949	41·023	41·097	41·171	41·245

Table for the Conversion of Specific Gravities—Continued.

Sp. gr.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
1·40	41·318	41·392	41·466	41·539	41·612	41·685	41·758	41·831	41·904	41·977
41	42·049	42·122	42·194	42·266	42·338	42·410	42·482	42·554	42·626	42·698
42	42·769	42·840	42·912	42·983	43·054	43·125	43·196	43·267	43·338	43·409
43	43·479	43·550	43·620	43·690	43·760	43·830	43·900	43·970	44·040	44·110
44	44·179	44·248	44·318	44·387	44·456	44·525	44·594	44·663	44·732	44·801
1·45	44·869	44·938	45·007	45·075	45·143	45·211	45·279	45·347	45·415	45·483
46	45·551	45·619	45·687	45·754	45·821	45·888	45·955	46·022	46·089	46·156
47	46·223	46·290	46·357	46·423	46·489	46·555	46·621	46·687	46·753	46·819
48	46·885	46·951	47·017	47·083	47·148	47·213	47·279	47·344	47·409	47·474
49	47·539	47·604	47·669	47·734	47·799	47·863	47·928	47·992	48·056	48·120
1·50	48·184	48·248	48·312	48·376	48·440	48·503	48·567	48·631	48·694	48·757
51	48·820	48·884	48·947	49·010	49·073	49·136	49·199	49·262	49·325	49·387
52	49·449	49·512	49·574	49·636	49·698	49·760	49·822	49·884	49·946	50·008
53	50·069	50·131	50·193	50·254	50·315	50·376	50·437	50·498	50·559	50·620
54	50·681	50·742	50·803	50·864	50·924	50·984	51·045	51·105	51·165	51·225
1·55	51·285	51·345	51·405	51·465	51·525	51·584	51·643	51·703	51·763	51·822
56	51·881	51·940	51·999	52·058	52·117	52·176	52·235	52·294	52·353	52·411
57	52·469	52·528	52·587	52·645	52·703	52·761	52·819	52·877	52·935	52·993
58	53·051	53·109	53·167	53·225	53·282	53·339	53·397	53·454	53·511	53·568
59	53·625	53·682	53·739	53·796	53·853	53·909	53·966	54·023	54·079	54·135
1·60	54·191	54·248	54·304	54·360	54·416	54·472	54·528	54·584	54·640	54·696
61	54·751	54·807	54·863	54·918	54·973	55·028	55·083	55·138	55·193	55·248
62	55·303	55·358	55·413	55·468	55·523	55·577	55·632	55·687	55·742	55·796
63	55·850	55·904	55·958	56·012	56·066	56·120	56·174	56·228	56·282	56·336
64	56·389	56·443	56·497	56·550	56·603	56·656	56·709	56·763	56·816	56·869
1·65	56·922	56·975	57·028	57·081	57·134	57·186	57·239	57·292	57·344	57·396
66	57·448	57·501	57·553	57·605	57·657	57·709	57·761	57·813	57·865	57·917
67	57·968	58·020	58·072	58·124	58·175	58·226	58·278	58·329	58·380	58·431
68	58·482	58·533	58·584	58·635	58·686	58·737	58·788	58·839	58·890	58·940
69	58·990	59·041	59·092	59·142	59·192	59·242	59·292	59·342	59·392	59·442
1·70	59·492	59·542	59·592	59·641	59·691	59·741	59·791	59·840	59·890	59·939
71	59·988	60·038	60·087	60·136	60·185	60·234	60·283	60·332	60·381	60·430
72	60·478	60·527	60·576	60·625	60·673	60·721	60·770	60·818	60·866	60·914
73	60·962	61·010	61·058	61·106	61·154	61·202	61·250	61·298	61·346	61·394
74	61·441	61·489	61·537	61·585	61·632	61·679	61·727	61·774	61·821	61·868
1·75	61·915	61·962	62·009	62·056	62·103	62·150	62·197	62·244	62·291	62·337
76	62·383	62·430	62·477	62·523	62·569	62·615	62·662	62·708	62·754	62·800
77	62·846	62·892	62·938	62·984	63·030	63·075	63·121	63·167	63·213	63·258
78	63·303	63·349	63·395	63·440	63·485	63·530	63·576	63·621	63·666	63·711
79	63·756	63·801	63·846	63·891	63·936	63·980	64·025	64·070	64·115	64·159
1·80	64·203	64·248	64·293	64·337	64·381	64·425	64·469	64·514	64·558	64·602
81	64·646	64·690	64·734	64·778	64·822	64·866	64·910	64·954	64·998	65·041
82	65·084	65·128	65·172	65·215	65·258	65·301	65·345	65·388	65·431	65·474
83	65·517	65·560	65·603	65·646	65·689	65·731	65·774	65·817	65·860	65·902
84	65·944	65·987	66·030	66·073	66·115	66·157	66·200	66·242	66·284	66·326
1·85	66·368	...	...	...	...	...	...	...	...	...

Other forms of hydrometer include the following:—

Cartier's hydrometer, in which 21° corresponds to 22° B., on the instrument for liquids lighter than water; above and below this point, 16° B. = 15° Cartier.

Beck's hydrometer, in which the point to which the instrument sinks in pure water is taken as zero, and that to which it sinks in a liquid of specific gravity 0·850 as 30°; one-thirtieth of the intermediate distance is taken as 1°, and graduations of this value are made both above and below the zero.

In *Baumé's hydrometer for liquids lighter than water*, the point to which the instrument sinks in a solution of one part of salt to nine parts of water is taken as 0°, and that to which it sinks in pure water as 10°. The distance between these points is divided into ten equal parts, and the graduations continued to the top of the spindle, the zero being placed at the bottom of the stem.

Degrees, Baumé, Cartier, and Beck.	Baumé.	Cartier.	Beck.	Degrees. Baumé, Cartier, and Beck.	Baumé.	Cartier.	Beck.
	Sp. gr.	Sp. gr.	Sp. gr.		Sp. gr.	Sp. gr.	Sp. gr.
0	...	...	1·0000	36	0·8488	0·8439	0·8252
1	...	...	0·9941	37	0·8439	0·8387	0·8212
2	...	...	0·9883	38	0·8391	0·8336	0·8173
3	...	...	0·9826	39	0·8343	0·8286	0·8133
4	..	...	0·9770	40	0·8295	...	0·8095
5	...	...	0·9714	41	0·8249	...	0·8061
6	...	...	0·9659	42	0·8202	...	0·8018
7	...	...	0·9604	43	0·8156	...	0·7981
8	...	...	0·9550	44	0·8111	...	0·7944
9	...	...	0·9497	45	0·8066	...	0·7907
10	1·0000	...	0·9444	46	0·8022	...	0·7871
11	0·9932	1·0000	0·9392	47	0·7978	...	0·7834
12	0·9865	0·9922	0·9340	48	0·7935	...	0·7799
13	0·9799	0·9846	0·9289	49	0·7892	...	0·7763
14	0·9733	0·9764	0·9239	50	0·7849	...	0·7727
15	0·9669	0·9695	0·9189	51	0·7807	...	0·7692
16	0·9605	0·9627	0·9139	52	0·7766	...	0·7658
17	0·9542	0·9560	0·9090	53	0·7725	...	0·7623
18	0·9480	0·9493	0·9042	54	0·7684	...	0·7589
19	0·9420	0·9427	0·8994	55	0·7643	...	0·7556
20	0·9359	0·9363	0·8947	56	0·7604	...	0·7522
21	0·9299	0·9299	0·8900	57	0·7565	...	0·7489
22	0·9241	0·9237	0·8854	58	0·7526	...	0·7456
23	0·9183	0·9175	0·8808	59	0·7487	...	0·7423
24	0·9125	0·9114	0·8762	60	0·7449	...	0·7391
25	0·9068	0·9054	0·8717	61	...	...	0·7359
26	0·9012	0·8994	0·8673	62	...	...	0·7328
27	0·8957	0·8935	0·8629	63	...	...	0·7296
28	0·8902	0·8877	0·8585	64	...	...	0·7265
29	0·8848	0·8820	0·8542	65	...	...	0·7234
30	0·8795	0·8763	0·8500	66	...	...	0·7203
31	0·8742	0·8707	0·8457	67	...	...	0·7173
32	0·8690	0·8652	0·8415	68	...	...	0·7142
33	0·8639	0·8598	0·8374	69	...	...	0·7112
34	0·8588	0·8545	0·8333	70	...	...	0·7083
35	0·8538	0·8491	0·8292				

A comparison of these hydrometers with the specific gravity, for liquids lighter than water, at 12°·5, is given in the preceding table.

If the strength of a liquid, containing a dissolved substance, is to be determined by means of its specific gravity, the nature of all the constituents present must be known, and no foreign matter, which could affect the density, should be present. A qualitative chemical examination should therefore be made first, if necessary.

Hydrometers in actual use should be checked by comparison with reliable standard instruments, graduated in real specific gravities; if considerable exactitude is required, the range of specific gravities on the standards should be distributed over an extended series of up to nineteen spindles.

G. Müller[1] tried to avoid this by constructing a "differential hydrometer," which is provided with glass weights, by means of which the value of the graduations is altered in a definite manner; Lunge is of opinion that instruments of this character do not give satisfactory results.

For the determination of the density of solid substances, the volumemeters of Schumann,[2] Michaëlis, Thörner, and others are used.[3]

A very simple and quick method for the determination of the specific gravity of liquids consists in weighing the quantity delivered by an accurate pipette; the liquid must, of course, first be brought to the desired temperature. Ruber[4] weighs the liquid in the pipette for this purpose; the pipette is not graduated for delivery, but so that it contains exactly 20 c.c. from the point to a mark on the stem. More exact results are said to be obtained with pipettes surrounded by a Weinhold-Dewar vacuum jacket, but the necessary adjustment and manipulation is then less simple.

An instrument for determining the specific gravity of small quantities of liquid, called an *Areo-pyknometer*, has been devised by Eichhorn.[5] It is a hydrometer which contains a bulb, provided with a stopcock, between the spindle and the gravity-bob; the bulb holds 10 c.c., and is filled with the liquid under investigation. If the instrument is then immersed in distilled water at 17°·5 C., the specific gravity is indicated directly on the scale. A similar instrument has been described by Rubenstorff.[6]

Special hydrometers, such as alcoholometers, saccharimeters, acetometers, etc., have long been used in various industries, some of which are subject to official control. Similar instruments for the hydrometric examination of mineral acids, alkalis, and salts, made according to the

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[1] *Cf.* P. Fuchs, *Z. angew. Chem.*, 1898, **11**, 505.

[2] *Z. anal. Chem.*, 1884, **23**, 1887.

[3] *Cf.* "Cements," p. 698.

[4] *Chem. Zeit.*, 1903, **27**, 94.

[5] Ger. Pat. 49683.

[6] *Chem. Zeit.*, 1904, **28**, 889.

most reliable tables, have lately been introduced by G. Müller;[1] they are not, however, in very general use. Detailed temperature correction tables for these hydrometers, for nitric acid, sulphuric acid, hydrochloric acid, and ammonia, and also tables for a large number of liquids and solutions, have been compiled by P. Fuchs.[2] The tables of the Imperial German Standards Commission will be referred to in the section on "Sulphuric Acid" (p. 347).

The 2nd International Congress of Applied Chemistry (1896) passed the following resolutions regarding hydrometers:—[3]

1. The scales should be either in specific gravities, or in degrees Baumé, Brin, Balling, etc. The relation of these degrees to the specific gravities to be determined by an international committee.

2. For liquids with different capillary properties, special hydrometers, graduated accordingly, should be used; otherwise corresponding corrections must be made.

3. Readings should, as a rule, be taken at the intersection of the surface of the liquid with the stem of the hydrometer, without regard to the meniscus (*cf.* p. 156, Fig. 56). In the case of opaque liquids, where this is impossible, the readings of a hydrometer, which has not been specially calibrated for such liquids, must be corrected to give readings corresponding to the actual surface of the liquid.

4. Hydrometers should be provided with a centigrade thermometer, graduated from the zero-point.

5. One end of the spindle should be provided with a mark coinciding with the final graduation of the scale, in order to be sure that the scale does not change its position.

6. The total errors of a hydrometer should not be greater than one graduation of the scale.

Further regulations were adopted by the 6th International Congress of Applied Chemistry (1906), which bear chiefly on the construction of hydrometers; these include, as a general rule, that if hydrometers are not used at the normal temperatures (15° or 20° C.), the results must be reduced to the normal temperatures, by reference to the special tables prepared by the International Congress.[4]

Göckel[5] is of opinion that hydrometers should be marked, not only with the temperature at which they are to be used, but also with the temperature of the water taken as standard, and also with a statement as to whether the specific gravities refer to normal pressure (760 mm.) or to vacuum. The German Standards Commission calibrates hydrometers with reference to water at maximum density and at normal

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[1] *Chem. Zeit.*, 1898, **22**, 104.

[2] *Z. angew. Chem.*, 1898, **11**, 745 and 909.

[3] *Jahresber. f. chem. Tech.*, 1896, 1167.

[4] These tables have not yet been published.

[5] *Z. angew. Chem.*, 1903, **16**, 562.

pressure, for instance, $\frac{15^\circ}{4}$ (760). The weights of hydrostatic balances such as Mohr's and Westphal's, are, on the contrary, almost invariably adjusted for $\frac{15^\circ}{15}$ (760), and cannot, therefore, agree with officially controlled hydrometers. Both hydrometers and pyknometers should also always be marked with an indication whether they are to be read in the plane of the surface of the liquid or at the top of the capillary elevation.

K. Measurement of Pressure and of Draught: Pressure Gauges and Anemometers

The determination of the pressure of a current of gas is often necessary in the course of technical work, especially those relatively small differences of pressure which occur in chimneys, gas-generators, sulphuric acid chambers, and similar plant; indeed, many chemical processes can only be rationally conducted with the aid of regular measurements of this nature. Observations of the differences of pressure, registered by the instruments in use, are sometimes sufficient, whilst in other cases the velocity of the current of gas and the quantity of gas traversing the system in a given time are deduced from the observations by calculation.

Instruments which simply measure the statical difference of pressure between two adjacent spaces, usually between the inside of an apparatus and the external atmosphere, are called *Pressure Gauges* or *Manometers*. Those which measure dynamic differences, that is, which register the velocity of the current of gas directly, are called *Anemometers*. Only those forms of anemometer which depend on manometric principles will be considered; for the theory of the subject the reader is referred to text-books on Physics and Mechanics.

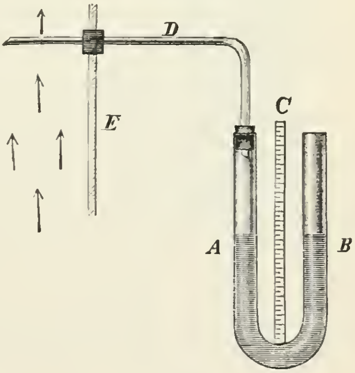

Fig. 57.

The simplest pressure gauges, which are for many purposes quite satisfactory for measuring small differences of pressure, consist of glass U-tubes (Fig. 57) provided with a scale C; one limb of the tube is in communication with the current of gas by means of the tube D, which is fixed through the wall E, whilst the other limb B is open to the outside air. If the pressure on the left-hand side of the wall is greater than on the right, the liquid will stand at a higher level in B than in A, and conversely.

Presssure gauges with a simple vertical tube, as shown in Fig. 57, are not sufficiently sensitive for the measurement of the draught in flues, etc., as a pressure of only 0·1 mm. of water corresponds to a velocity of 1·23 m. per second. The simplest apparatus for measuring such small differences of pressure, with greater accuracy, is the pressure gauge, with an inclined side tube, Fig. 58, designed by Péclet. It consists of a wide vessel A, communicating with a slightly inclined side tube B, provided with a corresponding scale. The tube is fixed to a vertical board, which is supported on a horizontal stand provided with levelling screws and a spirit-level, by means of which it can be brought into a horizontal position; the angle of inclination of the tube B is then easily determined. The liquid, either water or preferably alcohol, forms a very long meniscus in the tube B, the summit of which, if the tube has a diameter of 2-3 mm., is vertical to the cross-section of the latter, so that the readings are very easily made. If the tube has an inclination of 1 in 25, then each mm. on the inclined tube represents a difference of pressure of $\frac{1}{25}$ mm. in A; as the scale can be read to 0·5 mm., pressures of 0·02 mm. can be measured.

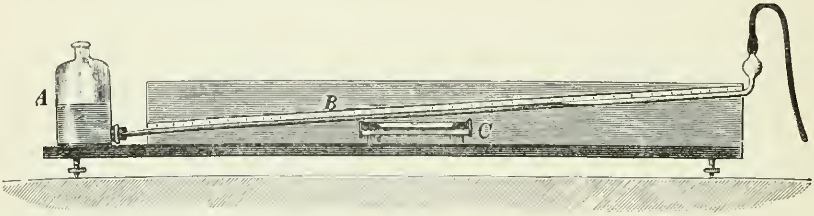

Fig. 58.

Alcohol is to be preferred to water as the registering liquid, both on account of its smaller coefficient of friction, and also because it returns to its original position much more quickly; the pressures must then, of course, be corrected in accordance with the specific gravity of the alcohol. If alcohol of 0·800 sp. gr. is used, 1 mm. corresponds to 0·8 mm. of water pressure.

The upper portion of the inner walls of the tube should be moistened before each experiment by inclining the instrument.

As the reduction of the readings from the angle of inclination in B to vertical pressure is only correct if the upper inner curvature of B is true, which is seldom the case with glass tubes, it is better to choose A of such a form that its internal diameter can be accurately measured, and then to calibrate B empirically. This is effected by delivering successive equal quantities of liquid, from a pipette, into B and noting the level after each addition; the height that each reading would correspond to in A can be easily calculated, knowing the volume of the liquid, and the diameter of A and the value of the scale on B, in vertical pressure, is thus obtained.

The position of the tube, connected with the pressure gauge, in the flue, and the angle at which it is inclined to the current of gas, are very important in all manometric measurements. The statical pressure is correctly indicated only when the opening of the connecting tube is at right angles to the direction of the current, as shown in Fig. 57; the pressure also varies at different points in the cross-section of the flue.

Accurate determinations of small differences of pressure can also be made by means of the *Differential Manometer*. One form of this instrument, designed by Seger, for the measurement of draught and of pressure, is shown in Fig. 59.

This consists of a calibrated glass U-tube A, both limbs of which end in large glass tubes B and C, of equal diameter. The tube B, A, C is fastened to a board, which also supports a sliding scale D, fixed parallel with one limb of A, and adjustable by means of slits *a a* and screw-pins *b b*. The U-tube is filled with two non-miscible liquids, of almost the same specific gravity, in such a way that their point of contact is near the zero of the scale.

Water and aniline or light petroleum spirit and dilute alcohol may be used, and it is preferable to colour one of the liquids. For the measurement of pressures greater than that of the atmosphere, the limb B, which is provided with a rubber stopper and glass tube, as shown, is connected by means of rubber, glass, or metal tubing with the flue or chimney to be tested, C being open to the atmosphere; if a pressure less than that of the atmosphere is to be measured, C is connected with the flue and B left open.

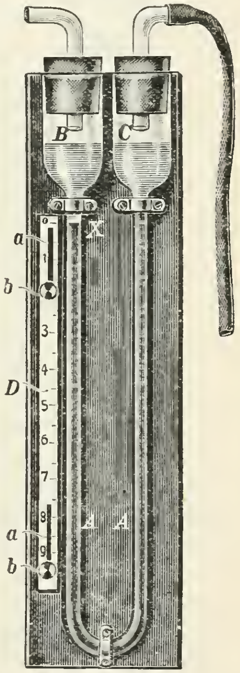

Fig. 59.

The apparatus is fixed vertically on a wall near to where the measurements are to be taken, and the scale adjusted so that its zero graduation is at the surface of contact of the two liquids; on then connecting B or C with the flue, etc., to be tested, a slight difference of level of the liquids in the upper wide portions of the two limbs will be produced. This difference is multiplied in the movement of the surface of contact of the liquids in A, in the ratio of the sectional areas of B and C, and that of the narrow tube A.

If, for instance, the sectional area of B and C is twenty times that of A, then a pressure-difference of 1 mm. will cause a displacement of the surface of contact X of 20 mm., so that very small differences of pressure are easily observed.

The divisions on the scale may be either empirical, if relative measurements only are required, or they may be made to correspond to water-pressure in mm., for more exact determinations; in the latter case, the graduations are calculated from the above ratio, and the specific gravities of the liquids used.

The sensitiveness and accuracy of the instrument increases with the ratio of the sectional areas of the upper vessels to that of the lower tube, and with the nearness in specific gravity of the two liquids employed.

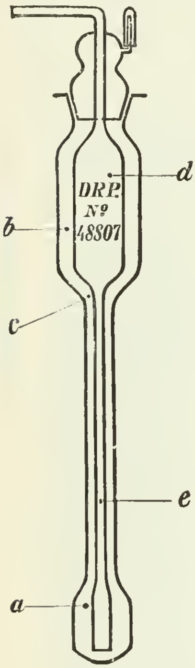

Fig. 60.

König's differential manometer, Fig. 60, depends on the same principle as the above. The two limbs of the tube are concentric, which facilitates the readings. A colourless liquid (mineral oil) and a red liquid (coloured alcohol) are supplied with the apparatus. It is filled by removing the inner tube, introducing about 10 c.c. of the red solution from a pipette, care being taken to avoid wetting the sides of the tube, until it reaches the point *a*, and then carefully pouring on the colourless liquid till it reaches *b*, without stirring up the red liquid below. The inner glass tube, to which a piece of rubber tubing has been attached, is then inserted as far as *c*, filled up to *d* with the upper liquid, by suction, and then pushed down into its final position, the liquid being meanwhile kept at the same height, by keeping the end of the attached tubing closed. To adjust the instrument, air is carefully blown in from above, so that one or two drops of the colourless liquid pass into the lower red solution, until the surface of contact of the two liquids stands at *e*. Should this point be passed, the upper tube must be lifted out as far as *c* and the operation repeated. The exact adjustment to the zero of the scale is effected by means of a stud, after fixing the instrument in its stand. Neither the instrument nor the stock solutions should be exposed to direct sunlight. The apparatus is cleaned by rinsing with concentrated sulphuric acid, washing with water, and drying carefully. As the point of contact of the liquids changes with the temperature, it must be brought to zero before each determination. It is advantageous to fit the apparatus with a three-way tap, which is ordinarily turned so that the interior of the apparatus communicates with the external atmosphere; the instrument is first adjusted to zero with the tap in this position, before each observation, and then turned through a right angle to establish connection with the space to be examined, the reading taken, and the tap finally turned back to its original position.

Lunge states that this instrument works very well, and that it is more convenient than Seger's apparatus.

Langen's manometer, modified by Lux,[1] Fig. 61, also depends on the principle, that if two tubes of unequal diameter communicate, then, on disturbing the equilibrium, the alterations in level of a liquid in the two tubes are inversely proportional to their cross-sections. When the difference in the cross-sections is sufficiently great, the alteration of level in the wide tube may be neglected, and the pressure measured by observing the narrow tube only. Five modifications of this apparatus are made, which are arranged for the measurement of high and low pressures and of reduced pressures; it is a convenient instrument, but it is not suitable for measuring very small differences of pressure.

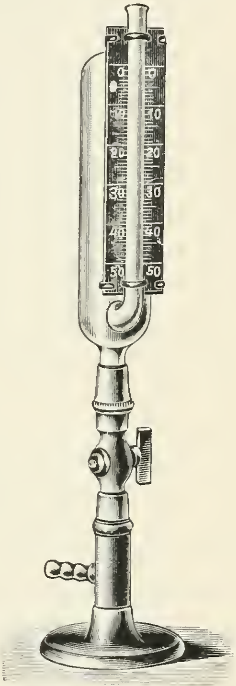

FIG. 61.

The velocity of a current of gas can be calculated from the pressure indicated by a manometer. According to Péclet,[2] for a gas at a small excess of pressure E, the velocity,

$$V = 396 \phi \sqrt{\frac{E}{E+B} \cdot \frac{1+\alpha t}{\delta}}$$

where E is the pressure, in terms of a column of water, indicated by the manometer, B the barometric pressure, also in terms of a column of water (*i.e.*, the height of the mercury barometer × 13·59) t, the temperature, and δ, the density of the gas.

The value of ϕ varies with the form of the aperture through which the gas escapes. For example, for atmospheric air at 0° and 760 mm. barometric pressure (*i.e.*, B = 10·334 m.) the relations between the velocity V, in metres per second, and the excess of pressure E, in metres are:—

E	1	0·1	0·01	0·001	0·0001	0·00001 m.
V	117·61	38·763	12·283	3·895	1·232	0·38952 m.

An excess of pressure of $\frac{1}{100}$ mm. indicates, accordingly, a velocity of almost 0·4 metres per second.

For holes in thin plates the value for ϕ is 0·65; for cylindrical apertures, 0·83; for convergent, conical apertures, 0·83 to 0·65, according to the angle; and for apertures which first contract a little and then

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[1] *J. Gasbeleucht*, 1890, **33**, 217; 1891, **34**, 288.

[2] *Ser. physique industrielle*, 1, 249.

expand towards the outside (Fig. 62), the relation to the angle α is as follows :—

Value of α	0°	1°	3°	5°	7°	9°	20°	30°	50°
„ ϕ	1·00	1·24	1·70	2·25	2·45	1·95	1·30	1·18	1·05

Thus the maximum is at 7° C., and is four times as great as the velocity from an opening in a thin plate.

When a manometer is connected to the interior of the current of gas by a cylindrical tube, with an opening placed vertically in the direction of the current, as is very usually the case in practice, the value of ϕ may be taken as $= 1$, and accordingly the velocities, in metres per second, are given directly by the above table.

It is to be borne in mind that the velocity varies in different parts of the cross-section of the chimney, and therefore, in order to obtain a mean value, a series of readings should be taken by moving the tube D (Fig. 57, p. 165) backwards and forwards; from such determinations the volume of gas passing up the chimney can be calculated, by multiplying the average velocity by the sectional area.

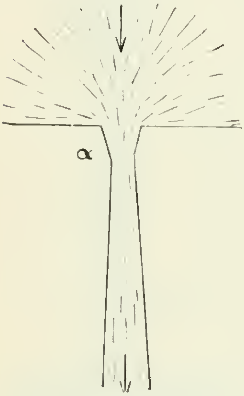

Fig. 62.

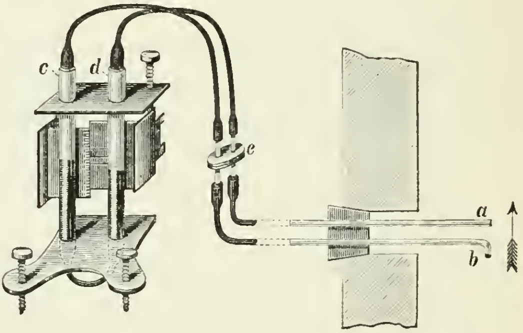

Fig. 63.

The dynamic method of measuring differences of pressure, as initiated by Péclet in his differential anemometer, consists in placing both limbs of the manometer in communication with the current of gas, the opening of the one connecting tube being placed vertically to, and that of the other parallel to, the direction of the current. In this case it is not the pressure-difference between the current and the outside air which is measured, but that between the static and dynamic pressure in the current itself. The method is very delicate, and serves for the direct measurement of the velocity of the current.

Fletcher has constructed an anemometer on this principle, which has been improved and simplified by Lunge.

It consists of two glass or brass tubes *a* and *b* (Fig. 63), which are fixed air-tight, by means of a cork, into a suitable opening in the channel or chimney, in which the velocity of the gas is to be measured, so that their ends are rather less than one-sixth of the distance of the diameter of the flue from its inner wall. The tube *a*, with the straight end, must be fixed as exactly vertical as possible to the direction of the current, whilst the tube *b* must be so fixed that the gas blows straight into its open end. These tubes communicate, by means of rubber tubing, with the U-tube *cd*, which is half-filled with ether. The current of gas produces suction at *a* and pressure at *b*; consequently the ether rises in *d* and falls in *c*. The difference in level between the ether columns in *c* and *d* is measured by means of a millimetre scale and vernier; this is called the "anemometer reading." By turning the sliding disc *e* through 180°, *a* is connected with *c* and *b* with *d*; the currents being thus reversed, an equal difference of levels, but in the opposite direction, should be recorded, which serves as a check on the first reading and should be identical with it.

The following tables serve for the calculation of the velocity of the current from the anemometer readings.

I.—Table for the Reduction of the Anemometer Readings to Velocity of Current, expressed in feet per second.

Column *a* gives the anemometer readings in inches; column *b* the velocity in feet per second at a temperature of 15° C. = 60° F., and barometric pressure 760 mm. = 29·92 inches.

a. Inches.	*b.* Feet per sec.	*a.* Inches.	*b.* Feet per sec.	*a.* Inches.	*b.* Feet per sec.	*a.* Inches.	*b.* Feet per sec.
·01	2·855	·16	11·42	·32	16·15	·95	27·83
·02	4·038	·17	11·77	·34	16·65	1·00	28·55
·03	4·945	·18	12·11	·36	17·13	1·25	31·93
·04	5·710	·19	12·45	·38	17·60	1·50	34·97
·05	6·384	·20	12·77	·40	18·06	1·75	37·77
·06	6·993	·21	13·08	·45	19·15	2·00	40·37
·07	7·554	·22	13·39	·50	20·18	...	...
·08	8·075	·23	13·70	·55	21·17	...	...
·09	8·565	·24	13·99	·60	22·12	...	...
·10	9·028	·25	14·28	·65	23·02	...	...
·11	9·469	·26	14·56	·70	23·89	...	...
·12	9·891	·27	14·84	·75	24·73	...	...
·13	10·29	·28	15·11	·80	25·54	...	...
·14	10·68	·29	15·38	·85	26·32	...	...
·15	11·06	·30	15·64	·90	27·08	...	...

II.—Table for the Reduction of the Anemometer Readings to Velocity of Current, expressed in metres per second.

Column *a* gives the anemometer readings in millimetres ; column *b* the velocity in metres per second at a temperature of 15° C., and barometric pressure 760 mm.

a. mm.	*b.* m.	*a.* mm.	*b.* m.	*a.* mm.	*b.* m.	*a.* mm.	*b.* m.	*a.* mm.	*b.* m.	*a.* mm.	*b.* m.
0·1	0·575	1·4	2·040	2·7	2·833	5·0	3·855	10·0	5·452	19·0	7·515
0·2	0·771	1·5	2·111	2·8	2·885	5·2	3·931	10·5	5·586	20·0	7·710
0·3	0·944	1·6	2·181	2·9	2·935	5·4	4·006	11·0	5·718	21	7·900
0·4	1·090	1·7	2·248	3·0	2·986	5·6	4·080	11·5	5·846	22	8·086
0·5	1·205	1·8	2·313	3·2	3·077	5·8	4·152	12·0	5·972	23	8·268
0·6	1·341	1·9	2·376	3·4	3·179	6·0	4·223	12·5	6·095	24	8·446
0·7	1·442	2·0	2·438	3·6	3·271	6·5	4·395	13·0	6·216	25	8·620
0·8	1·560	2·1	2·498	3·8	3·361	7·0	4·561	13·5	6·334	30	9·443
0·9	1·636	2·2	2·557	4·0	3·448	7·5	4·721	14·0	6·450	35	10·199
1·0	1·724	2·3	2·615	4·2	3·569	8·0	4·876	15·0	6·677	40	10·903
1·1	1·808	2·4	2·671	4·4	3·616	8·5	5·026	16·0	6·896	45	11·565
1·2	1·889	2·5	2·726	4·6	3·698	9·0	5·172	17·0	7·108	50	12·190
1·3	1·966	2·6	2·779	4·8	3·777	9·5	5·314	18·0	7·314	...	...

III.—Table for Correction for the Temperature at which the Anemometer Readings are made, to 15° C. = 60° F.

Column *a* gives the observed temperature ; column *b*, the factor by which the values in column *b* of Tables I. and II. must be multiplied, to give the correct velocity.

a. t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*
− 10	1·046	18	0·995	42	0·956	66	0·922	140	0·835	260	0·735
− 5	1·036	20	0·991	44	0·953	68	0·919	150	0·825	270	0·728
0	1·027	22	0·988	46	0·950	70	0·916	160	0·815	280	0·721
2	1·022	24	0·985	48	0·947	75	0·912	170	0·806	290	0·715
4	1·020	26	0·981	50	0·944	80	0·903	180	0·797	300	0·709
6	1·016	28	0·978	52	0·941	85	0·899	190	0·788	320	0·697
8	1·012	30	0·975	54	0·938	90	0·890	200	0·780	340	0·685
10	1·009	32	0·972	56	0·935	95	0·884	210	0·772	360	0·676
12	1·005	34	0·968	58	0·933	100	0·878	220	0·764	400	0·654
14	1·003	36	0·965	60	0·930	110	0·867	230	0·756	450	0·631
15	1·000	38	0·962	62	0·927	120	0·856	240	0·749	500	0·603
16	0·998	40	0·959	64	0·924	130	0·845	250	0·742	...	...

L. MEASUREMENT OF TEMPERATURE

The treatment of this subject is restricted to certain general considerations and to the description of a few typical instruments for the measurement of temperature. For further details the reader is recommended to consult text-books on Physics and the following works:—

High Temperature Measurements, H. le Chatelier, trans. by G. K. Burgess, 2nd edition, 1904; *Introduction to the Study of Metallurgy*, Sir W. Roberts-Austen, 5th edition, 1902; the article on "Thermometry" in the *Dictionary of Applied Chemistry*, by Thorpe and Muir; *Chemische Technologie der Brennstoffe*, F. Fischer (1880-1897), and *Chemisch-technische Analyse*, Post; the subject is also dealt with in the section on "Clay," p. 568.

Temperature measurements may be divided into the two groups, *Thermometry* and *Pyrometry*; the first includes the measurement of temperatures for which a mercury thermometer can be used, the second, high temperature measurements. Recent developments of technology may now also necessitate the measurement of temperatures below the scales of the mercury or alcohol thermometer.

Thermometry.—The mercury thermometer is almost invariably used for thermometric purposes in technical work; alcohol thermometers are used occasionally, but necessarily only for temperatures up to about 50°, and they are not to be regarded as very exact. With ordinary mercury thermometers, the limit of temperature that can be measured is at most 300°, owing to the unavoidable change in the capacity of the bulb, as the boiling point of mercury (360°) is approached. By filling the upper space of the thermometer tube with nitrogen, under pressure, and by the selection of suitable glass, mercury thermometers are made which can be used up to 550°; very long, ordinary thermometers, placed vertically, so that the mercury column exerts considerable pressure, may be used up to and above 360°.

Thermometers are very seldom checked by physical methods, in technical laboratories; it is usually sufficient to compare them with one or more standard instruments; such comparison is especially desirable when thermometers have been exposed to high temperatures for long periods. Corrections for the unexposed portion of the mercury column are not usually applied in technical work.

It is often necessary to employ special forms of thermometers for technical purposes, particularly instruments in which the bulb is situated at some distance from the scale; thermometers with bent tubes, etc., are also necessary at times. The bulb and tube must often be protected by a sheath, so as to guard against mechanical injury or fracture through sudden heating. If a perforated metal tube or other similar arrangement is used for this purpose, the thermometer will indicate the temperature fairly accurately, but if an unperforated sheath has to be used, the readings are always too low, even if the sheath is filled up with mercury, copper filings, etc., as should always be done. Some mechanical protection is afforded by wrapping asbestos round the exposed portions of the thermometer, but this considerably decreases the sensitiveness.

In order to ascertain that the temperature to be measured is not too high for the use of a mercury thermometer, a very practical suggestion, due to Weinhold, is to first place a piece of lead at the spot where the temperature measurement is to be made; the melting point of lead is 323°, and if the test-piece does not show any softening at the edges, even after some time, the mercury thermometer can be safely used.

In cases where frequent readings are not required, and no small rapid variations of temperature need to be observed, Weinhold recommends the use of the thermometer block (Fig. 64). This is made of cast iron or of copper, with an obliquely bored cavity *h*, which is half-filled with mercury, and provided with a perforated knob *k*; it is introduced into the flue, etc., to be tested, through a suitable opening, by means of wire passed through the slit in the knob. The block is left in position for ten to fifteen minutes, then quickly withdrawn, and a small thermometer, which has previously been warmed to about the required temperature, at once placed in the cavity *h*; the reading is taken when the thermometer reaches the highest point and the mercury begins to fall.

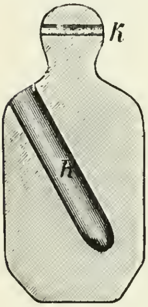

Fig. 64.

Many forms of recording thermometers, for automatically registering temperatures in drying chambers and the like, at a distant point, are in use; these all depend on the electrical transmission of the readings.

Pyrometry.—The following methods are in practical use for high temperature measurements:—

1. *High temperature Thermometers.* Mercury thermometers, filled with nitrogen under pressure, may be used up to 550°, as stated above.

Kühn[1] has drawn attention to the fact that works' thermometers, made for use up to 550°, which are often several metres long, are graduated for immersion to a definite position, which should always be adhered to in making observations. Also, that they may register up to 30° too high, or from 50° to 200° too low, after being used for some time; the former error is due to a contraction of the bulb, arising from the instrument having been insufficiently "aged" after manufacture. Low readings arise from the expansion of the glass, which may be caused by overheating, due to the thermometer not having been properly adjusted to the right position, when in use. When thermometers are inserted to other points than those for which they are calibrated, a correction must be applied. Thermometers in which the

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[1] *Chem. Zeit.*, 1903, 27, 54.

mercury is replaced by a low-melting alloy of potassium and sodium are also used for high temperature measurements, but they are expensive, and very breakable.

2. *Expansion Pyrometers.* The expansion of solids is mainly made use of in metallic pyrometers. One of the most usual forms, which can be used up to 900°, is that of Gauntlett and Desbordes,[1] in which the difference in expansion of a cast-iron and of a copper tube is measured. Steinle and Hartung's graphite pyrometer is a conjunction of graphite, which is assumed not to expand on heating, and metal; it is graduated up to 1200°, and was formerly generally used in Germany.

The coefficient of expansion of metals alters after frequent and prolonged heating, and therefore no expansion pyrometers are really reliable; they must accordingly always be compared with a standard instrument at frequent intervals.

The expansion of vapours and the measurement of the resulting pressure is made use of in the *Thalpotasimeter* devised by Klinghammer. This consists of a narrow tube, bent into the form of an S above, and closed below. The whole of the shorter, and two-thirds of the longer limb are filled with a liquid, the vapour pressure of which is measured on a manometer, thus indicating the temperature. The liquids used are liquid carbon dioxide for temperatures between −65° and 12°·5; liquid sulphur dioxide, for from −10° to +100°; dry ether, for from +35° to 120°; distilled water, for from 100° to 226°; high-boiling petroleum oil, for from 216° to 360°; and mercury, for from 357° to 780°.

3. *Air Pyrometers.* Many forms of air pyrometer are in use, in which the pressure caused by the expansion of air is measured. The instruments used by physicists are much too complex for technical purposes, for which, however, special forms have been devised, notably those of Wiske,[2] F. Fischer,[3] Knöfler,[4] and Heisch and Folkard.[5]

A distinct variety of air pyrometer comprises those in which the difference of pressure between ordinary and heated air is measured, as in the instruments of Wiske[6] and of Wiborgh.[7] The latter is provided with a correction for the atmospheric temperature and pressure, and gives accurate results, but a special, though simple manipulation is necessary before each observation, so that it is not suitable for continuous readings.

Another form of air pyrometer is that of Victor Meyer and Riddle,[8] in which the air is expelled from a heated platinum or porcelain vessel

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[1] Made by Schäffer & Budenberg, Manchester.

[2] Ger. Pat. 9681.

[3] *Z. angew. Chem.*, 1890, **3**, 591.

[4] Ger. Pats. 40081 and 43603.

[5] *Cf.* Hurter, *J. Soc. Chem. Ind.*, 1886, **5**, 634.

[6] Ger. Pat. 10065.

[7] *Ibid.*, 43958; *J. Soc. Chem. Ind.*, 1889, **8**, 214; *Stahl. u. Eisen*, 1891, **11**, 915.

[8] *Ber.*, 1893, **26**, 2443 and 3100; 1894, **27**, 3129.

by means of hydrochloric acid gas, and measured, after absorption of the latter.

4. *Fusion point Pyrometers.* Temperature determinations, by observation of the fusion of alloys, were first made by Prinsep in 1828, and have been extended by others, many special forms of apparatus having been constructed for this purpose. For high temperatures, the non-oxidisable metals, silver, gold, platinum, palladium, and their alloys, are used, the melting points of which have been determined by Erhard and Schertel, Holborn and Wien, Violle, Heycock and Neville, Harker, and others.

The alteration of clay by shrinking is the basis of the oldest pyrometer, that of Wedgwood (1782), which for nearly a century was the only guide for the measurement of high temperatures; it is now completely replaced by more reliable methods, of which the standard "cones" introduced by Seger[1] (1886) are the most important. These are known as "*Seger's fusible cones*," and are largely used, especially in the ceramic industries. They are small triangular pyramids, composed essentially of quartz, sand, felspar, calcium carbonate, and kaolin, the proportions of which are adjusted so as to give a series of fusion points at intervals of 20° to 30°. The fusion points of the mixtures, as determined by Hecht[2] by comparison with the Le Chatelier electric pyrometer, are given in the following table:—

Number of Cone.	Temperature. °C.	Number of Cone.	Temperature. C.	Number of Cone.	Temperature. °C.	Number of Cone.	Temperature. °C.	Number of Cone.	Temp. C.
022	590	010	950	3	1190	15	1430	27	1670
021	620	09	970	4	1210	16	1450	28	1690
020	650	08	990	5	1230	17	1470	29	1710
019	680	07	1010	6	1250	18	1490	30	1730
018	710	06	1030	7	1270	19	1510	31	1750
017	740	05	1050	8	1290	20	1530	32	1770
016	770	04	1070	9	1310	21	1550	33	1790
015	800	03	1090	10	1330	22	1570	34	1810
014	830	02	1110	11	1350	23	1590	35	1830
013	860	01	1130	12	1370	24	1610	36	1850
012	890	1	1150	13	1390	25	1630	...	...
011	920	2	1170	14	1410	26	1650	...	...

The standard cones, in sets of fifty-nine, which cover temperatures between 590° and 1890°, are made by the Royal Berlin Porcelain Works. Each cone is stamped, and a selection, according to the temperature to be measured, is placed in sequence, on a tile, at a point in the furnace which can be observed from the outside. The order of fusion is then noted, the final point being taken as the last of the series which is

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[1] *J. Soc. Chem. Ind.*, 1886, **5**, 489; *Thonindustrie Zeit.*, 1886, **10**, 135 and 229.

[2] *Thonindustrie Zeit.*, 1896, No. 18.

sufficiently fused for the summit of the cone, which being the thinnest portion is always softened first, to bend over so that it touches the tile; the fusion point of this cone is taken as the temperature of the furnace.

Kochs and Seyfert[1] have given "estimated" values for the temperatures of fusion of Seger cones, which are considerably higher than those of Hecht for the higher temperatures, but these can hardly be considered to be so reliable. Heraeus[2] determined the fusion point of cone number 36 = 1785° and number 37 = 1800° C.; that of corundum = 1865°.

Cone 26 is only fused by the highest temperatures which have so far been attained in technical furnaces, with the exception of electric furnaces; it corresponds to the minimum melting point of "fire-proof" clays. The cones 27-36 go up to the melting point of platinum, and are mainly used for determinations of the fire-resisting properties of clays.

Wiborg's *Thermophone*[3] is constructed upon an entirely different principle. It consists of an explosive, surrounded by a fire-proof substance which is a bad conducter of heat, and is made up in the form of cartridges. If one of these is introduced into a furnace, the time which elapses before it explodes will vary with the temperature of explosion of the contained substance, the thickness of the covering, and the surrounding temperature. The latter is estimated by observation of the time interval between the introduction and explosion of the cartridge, and comparison with an empirically prepared table.

5. *Optical Pyrometers.*[4] Optical phenomena have been made use of in a variety of ways for pyrometrical purposes—either roughly, by observation of the colour of incandescent matter and comparison with a standard glass, or more accurately, in association with the spectroscope or polariscope. The "lunette pyrométrique" of Le Chatelier is fairly frequently used in France, but it cannot be regarded as an accurate or reliable instrument.

Hempel[5] has constructed a spectroscopic apparatus for high temperature measurements, depending on the principle that for one and the same substance the length of the spectrum increases with the temperature.

Wanner's optical pyrometer[6] depends on the photometric comparison of polarised light from a small electric incandescent lamp and the

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[1] *Z. angew. Chem.*, 1901, **14**, 721.

[2] *Chem. Zeit. Rep.*, 1902, 303.

[3] Eng. Pat. 6284, 1895; *J. Soc. Chem. Ind.*, 1896, **15**, 377. The cartridges are supplied by Dr H. Geissler, Nachfolger, Bonn.

[4] A valuable and full monograph on *Optical Pyrometry*, by C. W. Waidner and G. K. Burgess, has been published by the U.S. Bureau of Standards, Bulletin No. 2, 1905, pp. 189-254.

[5] *Z. angew. Chem.*, 1901, **14**, 237.

[6] *Ibid.*, 1902, **15**, 715; *cf.* also, W. Feld, *Chem. Ind.*, 1903, **23**, 256. The pyrometer is supplied by Messrs Townson & Mercer, London.

furnace, etc., under observation. The instrument is arranged like a telescope; it is easy to manipulate, and is strongly to be recommended for estimating temperatures above 1500° C.; Le Chatelier's instrument is useless above this temperature, and the Wanner pyrometer has the further advantage, that it is better adapted for observing temperatures at points situated at some distance from the walls of a furnace.

In the Féry radiation pyrometer[1] or thermo-electric telescope the radiation from an incandescent body is focussed, either by a mirror or by a system of lenses, on to a small and sensitive thermo-couple; the electromotive force generated by the raising of the temperature of the couple is recorded by a sensitive potential galvanometer placed in series with the couple, the scale of which is divided so as to give direct temperature readings. The pyrometer is in the form of a telescope, and is supplied to cover various ranges of temperature from 900° up to 3500°. The readings are independent of the distance of the pyrometer from the furnace, and are uninfluenced within wide limits by the size of the hot body or observation hole under examination.

6. *Calorimetric Pyrometers.* Of the many forms of calorimetric pyrometers for gases, that of Bradbury is designed to measure the temperature of a hot-air blast, by mixing the gas with nine times its volume of air; the temperature of the mixture is determined with a thermometer and multiplied by ten. Values obtained by this method can only be approximately correct.

Methods in which a solid is exposed to the source of heat, and the absorbed heat determined calorimetrically, are much more important. The method, if correctly employed, gives good results, and it was formerly used for the control of other forms of pyrometer previous to the introduction of thermo-electric pyrometry.

The principle of the methods is as follows:—A small cylinder of iron, copper, or preferably of platinum, is placed in the furnace in a suitable receptacle. When it has remained there long enough to acquire the temperature of its environment, it is removed and dropped as quickly as possible into a definite quantity of water, the rise of temperature of which is measured with all the precautions necessary in calorimetric work. The temperature, T, of the furnace is then found from the equation:—

$$T = t' + \frac{p'(t' - t)}{pc}$$

where t = the initial temperature of the water; t' = the final temperature of the water; p' = the "water-equivalent" of the calorimeter, includ-

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[1] *Comptes rend.*, 1902, **134**, 977. The pyrometer is supplied by the Cambridge Scientific Instrument Co., Cambridge.

ing the contained water; p = the weight of the metal cylinder, and c = its specific heat at the temperature T.

Various forms of these pyrometers are in use for technical purposes, in which p and p' are constant, so that a simple factor can be employed to facilitate the calculations. In Siemens' copper pyrometer there is a special scale, which gives the temperature corresponding to the readings on the thermometer directly. Instruments graduated in this way are, however, only suitable for rough determinations; for more exact measurements more accurate apparatus must be used, and the results calculated as above.

7. *Electric Resistance Pyrometers* utilise the changes in the electric resistance of metals, with the temperature for pyrometric measurements.

In the Siemens resistance pyrometer, a platinum wire of a very high degree of purity is wound spirally, in a corresponding groove, round an earthenware cylinder which is contained in a strong cast-iron tube, closed below, and is insulated from the tube by means of asbestos. The spiral wire has a diameter of 0·4 mm., and is joined to three thicker wires, which are of equal thickness; one of these is fused to one end, and two to the other end, of the spiral wire. These thicker wires are protected by thin earthenware tubes, which are placed in the further end of the same iron tube that carries the spiral; only the portion of the tube containing the spiral is placed in the furnace. The thick platinum wires are attached by copper wires to a differential voltameter, which is connected with a fairly strong galvanic battery. The current of the latter is divided between two circuits, of which each passes through one of the voltameters, one of them through a known resistance in addition, and the other through the resistance to be measured. As the currents in the two circuits are inversely proportional to the resistances, and the quantities of gas generated in the voltameters are directly proportional to the current strengths, the ratio of the quantities of electrolytic gas is the inverse ratio of the resistances. From this comparison the temperature is determined by reference to a specially constructed table.

This pyrometer was for a long time regarded as a very reliable and standard instrument, and its utility was widely recognised. As the result, however, of special investigations, it has had to forego this claim, it having been fully established that it is liable to changes of zero.[1]

A modified resistance pyrometer, in which due precautions are taken to eliminate the sources of error of the Siemens pyrometer, has since been devised by H. L. Callendar.[2] In this instrument, the platinum wire is wound on a mica frame and connected by stouter wires, either to

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[1] *Cf.* Report by Committee of the British Association, *Reports*, 1874, 242.

[2] *Phil. Trans.*, 1887, **178**, 161. *Phil. Mag.*, 1891, **32**, 104; 1892, **33**, 220.

an indicator on which the temperature can be read directly, or to a recording drum. The resistance wire is enclosed in a porcelain, steel, or brass tube, according to circumstances, to protect it against fumes; a zero method is adopted for measuring the resistances with a galvanometer. Rapidly varying temperatures can be readily followed and measured, and the instruments are constructed for varying ranges of temperature, between low temperatures and 1400°.[1]

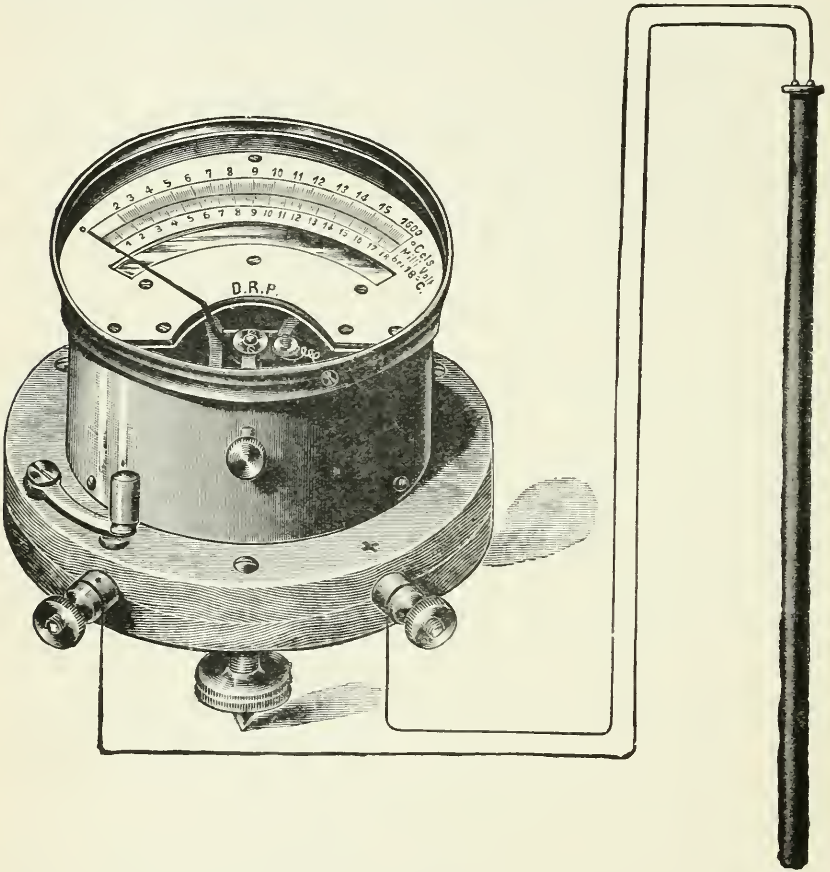

FIG. 65.

This instrument has been largely adopted for many forms of technical pyrometric determinations.

Resistance pyrometers, either with or without their accessory apparatus, are verified by the National Physical Laboratory.

8. *Thermo-electric Pyrometers.* Thermo-electricity was suggested for the measurement of high temperatures by Becquerel (1830) and

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[1] The Callendar pyrometer is made by the Cambridge Scientific Instrument Company, Cambridge.

by Pouillet (1836), but Le Chatelier[1] (1887) was the first to construct a really reliable and practical instrument, which can be used for the measurement of very high furnace temperatures, and also for the extremely low temperatures which have recently been obtained.

The working portion of the Le Chatelier pyrometer (Figs. 65 and 66) consists of a thermo-electric couple, formed of a wire of pure platinum, *a*, 0·6 mm. thick and 1·5 m. long, and a wire, *b*, of the same dimensions, made of an alloy of nine parts platinum to one part rhodium. The junction of the two wires, the temperature of which determines the strength of the current, must be made without the use of any foreign material; Le Chatelier unites the wires by twisting them together, whilst Heraeus and others adopt the more reliable method of fusing them together. Both wires are insulated by means of porcelain tubes, *c* and *d*, 1 m. long, which are protected in their turn by the iron tube *ee*, as shown in Fig. 66. In a reducing flame, a platinum carbide is formed which would alter the electromotive force; the porcelain tubes, which are glazed outside, prevent this action. The wires are connected up outside with platinum wires leading to a d'Arsonval galvanometer (Fig. 65), the needle of which gives readings on two scales. One of these indicates the electromotive force in volts, and the other the corresponding temperatures as determined by comparison with an air thermometer; the readings of the instrument on the former scale can, therefore, be easily controlled by comparison with a Clark's standard cell.[2]

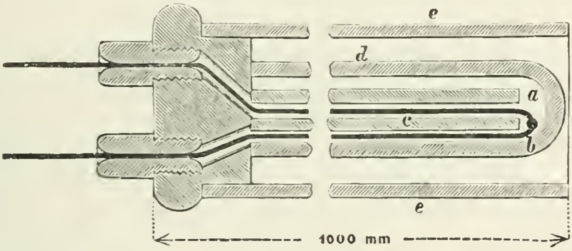

FIG. 66.

The National Physical Laboratory undertakes the verification of thermo-junction pyrometers at temperatures between 300° and 1300°.

Instead of the arrangement of porcelain and iron tubes, shown in Fig. 65, which is suitable for large furnaces, other forms can easily be made, adapted for use with crucibles, tubes, and other laboratory apparatus. One of the great advantages of this instrument is that it can be used equally well for the measurement of the temperature of

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[1] *Comptes rend.*, 1886, **102**, 819; *Bull. Soc. Chim.*, 1887, 47, 42.

[2] The Chatelier and other forms of thermo-electric pyrometers are made by the Cambridge Scientific Instrument Company, Cambridge.

either large or small masses of material, as it is only necessary to expose the thermo-junction *ab* to the temperature to be measured.

The galvanometer may be placed at a considerable distance from the furnace, etc., without the necessity of making any allowance for the resistance of the conducting wires—for instance, in the office of the works-manager—but it must be on a support free from vibration, such as a wall-bracket. If it is at such a distance from the thermo-couple that the external resistance of the circuit is essentially greater than 1 ohm., this must be allowed for in the calibration; for distances up to 100 m., insulated copper wire of 2 mm. diameter may be used as the conducting wire. The thermo-junction and the leads to the galvanometer should be practically at the atmospheric temperature; this can be effected, either by having a sufficiently long thermo-couple, or by special cooling.

Full precautions must be observed in the adjustment and use of the galvanometer; it must always be accurately centred and perfectly horizontal, as otherwise the needle will not come to rest at the zero-point of the scale. If the temperature of the cold junction is higher than that at which the instrument has been calibrated, the galvanometer scale must be moved from right to left by the number of degrees corresponding to this difference. Thus, if the junction is at 50° C., and the calibration has been effected at 0°, the temperature usually adopted in the verification of thermo-junction pyrometers by the National Physical Laboratory, the needle will, after correct adjustment, come to rest at the 50° graduation of the scale. As an alternative, this temperature difference may simply be added to the temperature found, with the galvanometer adjusted to the zero of the scale.

The thermo-couple should be chosen of such length that the terminals are so far from the furnace that their temperature does not much exceed that of the atmosphere. For technical purposes the relatively small difference in temperature is then usually disregarded, and the galvanometer readings as calibrated are considered to be sufficiently accurate. The thermo-couple should only be used without a protective sheath when contact with substances which might affect the incandescent platinum is excluded; any luminous flame has an injurious effect. If either of the wires of the thermo-couple breaks off, a satisfactory contact can be made by twisting the loose ends tightly together for a distance of about 1 cm. The thermo-junction of the two wires may be repaired similarly. For most technical purposes the thermo-couple should be mounted in a porcelain tube; one wire of the couple is then held in a narrow porcelain tube so that the thermo-junction projects just outside, whilst the other wire passes back along the outside of the tube, thus ensuring the insulation of the two wires from one another. The tube may, of course, be made up of several sections. A wider porcelain tube, glazed outside and closed at the bottom, serves to protect the couple from the action of furnace gases, etc. To protect the outer porcelain tube against mechanical injury and violent fluctuations of temperature, it is often advantageous to wrap it in asbestos fibre, and to place it in an outer tube of iron, nickel, or fire-clay. If metallic protecting tubes are used, care must be taken that they are not bent by the heating, and thus cause breaking of the porcelain tubes inside.

If the couple is to be left in the furnace for some time, this method of protection should always be adopted. No further precautions are necessary at temperatures below 1000°. Above this temperature the iron becomes white-hot, and may bend and break the porcelain tube within; the couple should in such cases be only left in the furnace for a short time, or the iron sheath should be supported on a fire-clay slab, or coated with fire-clay, or protected by a fire-clay tube.

The length of time necessary for a thermo-couple to attain a temperature of 700° is five minutes if protected by a porcelain tube only, and ten minutes if it is further wrapped in asbestos fibre and placed in an iron sheath. If practically immediate readings are required, the thermo-junction is left unprotected, and the main length of the wires protected as above; the thermo-junction becomes brittle in time, however, with this treatment, and must be re-joined.

Rapid fluctuations of temperature should be avoided; the tube should be slowly warmed before being placed in the furnace, and should be allowed to cool slowly after removal.

O. Pfeiffer[1] is of opinion that the fragile and expensive outer porcelain tube *d* (Fig. 66, p. 181) may be omitted altogether and the two wires of the couple passed through thin-walled porcelain tubes 1·2 m. long, 4 mm. external, and 2 mm. internal diameter. These are placed in an iron gas-pipe 1 cm. wide, and a little shorter than the porcelain tubes, so that the junction projects at one end, and the free space is filled in with asbestos fibre.

M. CALCULATION OF ANALYTICAL RESULTS

Means which shorten the calculations of analytical results, especially if they also contribute to the avoidance of error, greatly facilitate the work of a technical laboratory. Four-figure logarithms are not sufficiently accurate for most work, as the fourth place is uncertain, but five-figure logarithms almost always suffice. Ready-reckoners are preferred by many, and the slide-rule can be very advantageously used for many technical calculations. Tables specially calculated for chemical purposes, such as those given in books on Analytical Chemistry, and

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[1] *Z. angew. Chem.*, 1901, 14, 390.

reference tables, are a still more convenient adjunct for analytical calculations.[1]

Published tables are naturally not adapted for every class of work, and in many cases it is convenient to prepare special tables of factors, for specific calculations such as those given in the section on "Sulphuric Acid," or for use with the nitrometer (p. 146).

It is a general rule, in both scientific and technical analysis, to calculate to one, and only one figure, beyond that which can be regarded as significant. If a method is reliable to within one-tenth per cent., the percentage results should be given to not more than two places of decimals. If, however, an ore is valued in percentages only, it is often advisable to give the analytical result in whole percentages, or at most to one quarter or one-tenth per cent., so as to avoid confusion in the sales.

There are two quite different cases which must not be confused in this connection. If the main constituent of a substance, representing perhaps 50, 80, or 90 per cent. of the total, has to be determined, the percentage will practically never be given to more than two places of decimals, as even the first place will only be reliable in exceptional cases. In most other cases, also, it would be useless, or even misleading, to give the percentage to more than two places of decimals. But where a constituent has to be determined which only occurs in very small amount, such as gold in quartz, phosphorus in steel, ammonia in water, and the like, it is necessary to give the result to a hundredth or even to a thousandth per cent. of the original substance, provided the analytical methods employed are sufficiently accurate and a knowledge of the exact quantity is important.

The choice of the atomic weights to be used in calculating the results of analyses is an important consideration. New determinations are constantly being made, and within recent years many fundamental figures, *e.g.* the ratio $H : O = 1 : 15{\cdot}96$, which had long been considered absolutely reliable, have been found to need revision; nor can work in this direction be regarded as final. Many chemists are accordingly of the opinion that it would be an advantage to use approximate atomic weights for technical purposes, as these are less likely to be affected by subsequent determinations; others maintain that it is wrong in principle to use numbers which are really inaccurate, such as 197 instead of 197·2 for gold, which is certainly too low.

The rounded-off values were used in the former (German) edition of this work, largely because considerable differences of opinion existed as to the exact atomic weights of many of the elements. The table

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[1] Lunge recommends *Logarithmische Rechentafeln für Chemiker*, by F. W. Küster, 6th edition, 1906, which have been used throughout for the calculation of the figures given in this book, except for the volumes of gases, which have been calculated from the observed densities.

prepared by the International Committee on Atomic Weights, which is given below, has almost completely removed this objection to the use of the values, now regarded as the most accurate. The atomic weights are all given on the basis O = 16, as this is the only basis likely to be adopted internationally for analytical purposes, and a universal agreement of this character is of far greater importance for technical purposes than any theoretical advantages of the basis H = 1.

International Atomic Weights (1908).

		O = 16.			O = 16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	143·6
Argon	A	39·9	Neon	Ne	20
Arsenic	As	75·0	Nickel	Ni	58·7
Barium	Ba	137·4	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	191
Boron	B	11	Oxygen	O	16·00
Bromine	Br	79·96	Palladium	Pd	106·5
Cadmium	Cd	112·4	Phosphorus	P	31·0
Cæsium	Cs	132·9	Platinum	Pt	194·8
Calcium	Ca	40·1	Potassium	K	39·15
Carbon	C	12·00	Praseodymium	Pr	140·5
Cerium	Ce	140·25	Radium	Rd	225
Chlorine	Cl	35·45	Rhodium	Rh	103·0
Chromium	Cr	52·1	Rubidium	Rb	85·5
Cobalt	Co	59·0	Ruthenium	Ru	101·7
Columbium	Cb	94	Samarium	Sm	150·3
Copper	Cu	63·6	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	166	Silicon	Si	28·4
Europium	Eu	152	Silver	Ag	107·93
Fluorine	F	19·0	Sodium	Na	23·05
Gadolinium	Gd	156	Strontium	Sr	87·6
Gallium	Ga	70	Sulphur	S	32·06
Germanium	Ge	72·5	Tantalum	Ta	181
Glucinum	Gl	9·1	Tellurium	Te	127·6
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·0	Thallium	Tl	204·1
Hydrogen	H	1·008	Thorium	Th	232·5
Indium	In	115	Thulium	Tm	171
Iodine	I	126·97	Tin	Sn	119·0
Iridium	Ir	193·0	Titanium	Ti	48·1
Iron	Fe	55·9	Tungsten	W	184
Krypton	Kr	81·8	Uranium	U	238·5
Lanthanum	La	138·9	Vanadium	V	51·2
Lead	Pb	206·9	Xenon	Xe	128
Lithium	Li	7·03	Ytterbium	Yb	173·0
Magnesium	Mg	24·36	Yttrium	Yt	89·0
Manganese	Mn	55·0	Zinc	Zn	65·4
Mercury	Hg	200·0	Zirconium	Zr	90·6

When tables are employed, the use of exact figures, which is certainly of advantage, takes practically no more time than that of approximate numbers. If the latter are preferred, as being often sufficient for "practical" purposes, the values and factors given are easily rounded.

With regard to the formulation of analytical results, W. Fresenius[1] considers that it is most desirable that the formulæ of all constituents should be appended to their names; that the name of an acid should be understood to indicate the acid itself, and not its anhydride or characteristic ion; that if results are expressed according to the old dualistic notation, they should be written, "Sulphuric acid (anhydride) SO_3," or "Sulphuric acid, in terms of anhydride, SO_3," and so on; and that if expressed in ions, the names of the metals should be used, or in case of various stages of oxidation, such terms as "Mercurous-ion," "Mercuric-ion," and the anions expressed as "Sulphate-ion SO_4," etc.

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[1] *Fifth International Congress of Applied Chemistry*, 1903; *Z. angew. Chem.*, 1903, **16**, 539.

SPECIAL METHODS OF TECHNICAL ANALYSIS

TECHNICAL GAS ANALYSIS

By Professor F. FISCHER, Göttingen. English translation revised by
CHARLES A. KEANE, M.Sc., Ph.D.

THE analysis of gases is undertaken chiefly in connection with the examination of gaseous fuels and of combustion products. It also constitutes a most important method of analysis in the alkali industry, in the manufacture of illuminating gas, and in many other branches of chemical manufacture; the special methods that are employed in these cases are described under the respective sections.

In all branches of gas analysis the proper taking of the sample is quite as important as the method of analysis adopted. In the case of chimney gases, samples may be regarded as having a fairly constant composition if the charging is done by means of a hopper, or by some continuous mechanical process, but with ordinary intermittent charging the composition varies considerably: this is illustrated in the following data obtained in the firing of a boiler furnace :—

	1 Minute after Stoking.	12 Minutes later.
Carbon dioxide . .	13·5 per cent.	4·0 per cent.
Carbon monoxide . .	0 „	0 „
Oxygen . . .	5·5 „	16·5 „
Nitrogen . . .	81·0 „	79·5 „
Soot	Present.	0 „

In such an instance the analysis of a single sample is seldom of value. So-called *average samples* are equally unsatisfactory, because even when a constant method of suction is used for taking the sample, it is hardly possible to collect such a fraction for analysis as really represents the composition of the whole. Even were such a method reliable, analyses made from single samples obtained in this way would seldom be of use, and would, moreover, lead to wrong conclusions in respect to the working of a furnace. Such analyses, for instance, led Scheurer-Kestner[1] and Schwackhöfer[2] to the entirely

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[1] *Cf.* Fischer, *Chemische Technologie der Brennstoffe*, vol. i., p. 220.

[2] *Z. angew. Chem.*, 1887, 216; 1893, **6**, 398.

erroneous assumption that at least two to three times the volume of air, theoretically necessary, is required for complete combustion.

A reliable criterion of the course of a combustion can only be obtained by the analysis of a series of separate samples taken at successive short intervals; the effect of the stoking and similar influences can then be gauged. If the nature of the fuel is fairly well known, the possible presence of appreciable quantities of carbon monoxide and of other combustible gases can be judged from the total of carbon dioxide and oxygen that are present; in such cases the determination of the two latter gases suffices.[1]

In order to determine the small quantities of combustible gases which may occasionally be present in normal chimney gases, even accurate volumetric methods are insufficient, and gravimetric methods of analysis must be employed; these are carried out by drawing the sample for a sufficient length of time through a suitable absorption apparatus, whilst at the same time a gas-volumetric test is made every five or ten minutes, in order to follow the course of the combustion.[2]

An old method that serves as a rough criterion of the course of a combustion consists in inserting a burning splinter in the effluent gases; if it continues to burn, a large excess of oxygen is indicated. Schäffer and Budenberg,[3] and also Hempel,[4] have suggested placing a gas flame in the exit gases, as a similar indication.

Several forms of apparatus have been designed for the automatic examination of chimney gas. Of these the "*Ados*"[5] or "*Sarco*" apparatus, in which the carbon dioxide is determined by absorption, is extensively used. Other automatic forms of apparatus for the determination of the carbon dioxide in chimney gases are the Simmance-

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[1] Since $C + O_2 = CO_2$, the 21 per cent. of oxygen in air gives 21 per cent. of carbon dioxide; for the combustion of hydrogen every 2 kilos use up 11·15 cb.m. of oxygen. In the case of a coal having the composition:—

Carbon	84 per cent.
Hydrogen	4 ,,
Oxygen	8 ,,
Ash, water, etc.	4 ,,

the burning of 1 kilo involves the consumption of air required for 0·84 kilo carbon and 0·03 kilo hydrogen, the contained oxygen of the fuel sufficing for the combustion of the rest of the hydrogen. For every $\frac{84}{12} = 7 \times 22{\cdot}3 = 156{\cdot}1$ cb.m. of carbon dioxide formed, $\frac{3}{2} \times 11{\cdot}15 = 0{\cdot}75 \times 22{\cdot}3 = 16{\cdot}75$ cb.m. of oxygen disappear from the gaseous products, owing to the combustion of the hydrogen. If, therefore, the chimney gases contain 14 per cent. of carbon dioxide, the average free oxygen, when combustion is complete, will be $21 - \left(14 - \frac{16{\cdot}75 \times 14}{156{\cdot}1}\right) = 5{\cdot}5$ per cent. After a fresh stoking the proportion of free oxygen decreases to 4-5 per cent., but increases to 6-7 per cent. when the charge is spent. The analytical results should be in accord with these data, and should always be carefully checked if this is not the case.

[2] Cf. *Dingl. polyt. J.*, 1884, **251**, 323; *Fischer's Jahresber.*, 1835, **31**, 1295.

[3] *Z. angew. Chem.*, 1888, **1**, 167. [4] *Chem. Ind.*, 1886, **9**, 98.

[5] *Z. angew. Chem.*, 1905, **18**, 1231; Ger. Pat. 160288. The apparatus is supplied by Sanders, Rehders & Co., 108 Fenchurch St., London, E.C.

Abady "*Combustion Recorder*"[1] and the "*Autolysator*,"[2] of Strache, Johoda, and Genzken. H. le Chatelier[3] has suggested a rapid method for testing chimney gases, in which the ends of two insulated conducting wires are connected by a deposit of copper oxide, which is placed in the path of the chimney gases; if the air supply to the fuel is insufficient for complete combustion, the copper oxide is reduced to metallic copper, and an electric circuit is completed, either to a galvanometer or to an electric bell; if there is sufficient air, no reduction takes place and no current passes. F. Haber,[4] has designed an instrument by means of which the composition of chimney gases is estimated by the observation of the refractive power: it can be adapted for photographic registration as well as for direct reading, and is sensitive to differences of from 0·2 to 0·25 per cent. of carbon dioxide.

It has frequently been proposed to deduce the content of carbon dioxide from the specific gravity of the gases. Uehling and Steinhardt[5] have suggested the determination of the rate of effusion for this purpose; Lux and Precht[6] pass the gas through a hollow ball, which is subsequently weighed. Pfeiffer[7] and Arndt[8] draw the products through a suitable holder suspended on a balance, and Siegert[9] passes the gas through a hollow ball, which is arranged to swing on a balance, so that the pointer indicates the percentage of carbon dioxide directly. Results obtained by such methods can only be regarded as approximate values which may be of use as a check on the ordinary working of boilers and the like, because the specific gravity of the gases is not only dependent upon the carbon dioxide, but also upon the water-vapour, unburnt gases, etc., and is, moreover, variable with the pressure. A proper chemical examination is accordingly to be regarded as the only satisfactory method of analysis.

The Collecting of Samples

The collecting of samples is effected by withdrawing the gases from the flue or chimney, through connecting tubes, into a suitable containing vessel. The containing vessel may either form part of the gas-analysis apparatus, as is generally the case when the sample is submitted at once to analysis, or it may be an independent vessel suitable for transport. If the gas to be sampled is under pressure the filling of the vessel is easily effected, otherwise an aspirator must be

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[1] Eng. Pat. 18680, 1906. The apparatus is made by Alexander Wright & Co., Westminster, London.

[2] *Z. f. chem. Apparatenkunde*, 1907, **2**, 57. The apparatus is made by the Ver Fabriken für Laboratoriumsbedarf, Berlin.

[3] *Bull. Soc. d'Encourag.*, 1904, **106**, 471; *J. Soc. Chem. Ind*, 1904, **23**, 951.

[4] *Z. Electrochem.*, 1906, **12**, 519.

[5] *Fischer's Jahresber.*, 1896, **42**, 1166.

[6] *Ibid.*, 1893, **39**, 1205.

[7] D. R. P., No. 78612.

[8] *Ibid.*, Nos. 70829, 125470, and 129163.

[9] *Z. Verein. deutsch. Ing.*, 1888, **32**, 1090; 1893, **37**, 595.

employed; small indiarubber aspirators, such as that shown in Fig. 76 C (p. 199), and various forms of glass aspirators and water-pumps, are generally used.

Previously to collecting the sample, it is important to be certain that all air is removed from the connecting tubes and any other intermediary apparatus. The material of the connecting tube must be selected so as to resist the prevailing temperature, and it must be unaffected by the constituents of the gas. Glass tubes are used whenever possible; they can be safely employed for temperatures up to 500° or 600°. Above this, porcelain tubes are used; these necessitate gradual heating up, owing to their liability to crack. Iron and other metal tubes should be avoided; in presence of oxygen, iron tubes effect a considerable absorption of this gas, even at low temperatures, and give it off to reducing gases. It has been found, for instance, that in passing generator gases through iron tubes, heated to a dull red heat, the percentage of carbon dioxide increased from 1·5 to 26 per cent.[1] The connecting tubes are held in position by a perforated cork or rubber stopper, or by means of a suitable cement. Should there be any doubt that a well-mixed sample of the gases has not been obtained, further samples should be taken at some other point in the furnace or gas pipe.

To collect the gases from a Bessemer converter, F. Fischer[2] uses a porcelain tube (Fig. 67), placed inside an iron tube *b*, the two being held together at *a* by a collar of fireclay, and the porcelain tube projecting about 5 cm. beyond the iron tube. The porcelain tube is connected with the glass tube *z* at *c*, by a joint made with a mixture of clay and water glass; the glass tube is connected by rubber tubing *g*, to a series of bulbs *n*, the last of which is attached to a small rubber aspirator. To collect the sample, the tube is placed in an upright position over the mouth of the converter, so that it is in the centre of the current of gas; the sample is then aspirated through the bulbs, one of which is sealed off every two minutes.

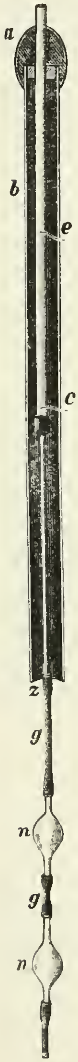

Fig. 67.

Apparatus for Storing Samples of Gases.—If the gas sample is not drawn directly into the gas-analysis apparatus, transport vessels are necessary. Glass bulbs of about 100 c.c. capacity (Fig. 68) are used, which are attached to the collecting tubes

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[1] Fischer, *Dingl. polyt. J.*, 1879, **234**, 528.

[2] *Z. Verein. deutsch. Ing.*, 1902, **46**, 1006 and 1367.

as described above (Fig. 67). After being filled, they are sealed off at *a*, on either side. Should it be necessary to seal off the tubes in the open, a small oil lamp (Figs. 70 and 71, in half actual size) may be advantageously used. It is provided with a wickholder *d*, and a metal cover B, having air-holes at the bottom *c*, a larger opening at the top, and a round hole *e* at the side, through which the blowpipe flame, blown from the blowpipe *n*, (to which a rubber tube and mouthpiece are attached) is directed.

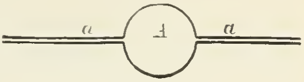

Fig. 68.

Fig. 69.

If the samples are only kept for a few hours before examination, light glass cylinders of about 100 c.c. capacity, provided with well-ground stopcocks at either end, may be used (Fig. 69). A convenient form of tube, in which a sample of gas can be sealed and subsequently withdrawn readily for analysis, is described by Sodeau.[1]

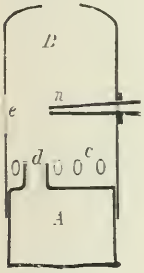

Fig. 70.

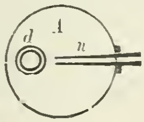

Fig. 71.

The gas sampler devised by Stead[2] (Fig. 72) is a very useful form of apparatus, by means of which the sample can be aspirated and subsequently readily transferred for analysis. The gas-collector H is provided with four stopcocks, of which C is attached to the reservoir A, by means of a stout piece of rubber tubing. The reservoir is filled with mercury or water, according to the nature of the sample to be taken. By placing the reservoir on the shelf B, and opening the taps C and D, the air in H is expelled and replaced by the mercury. The taps C and D are then closed, the connecting tube from the flue or chimney connected to E, and the reservoir lowered; by now opening D and E, the gas is drawn through the collecting tube and the upper tubes of the aspirator, thereby completely removing the contained air. D is then closed, the reservoir placed under the tap F, and the latter opened, when the mercury flows out, thereby drawing in the gas, the rate of entrance of the gas being regulated by the rate of flow of the mercury. After the sample has been collected, the taps are closed and the gas

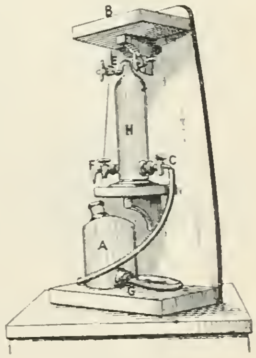

Fig. 72.

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[1] *J. Soc. Chem. Ind.*, 1903, **22**, 190.

[2] *Ibid.*, 1889, **8**, 176.

transferred for analysis, by placing the reservoir on B and opening the stopcocks C and D, sufficient gas being first allowed to escape to clear the connecting tubes. If the sample is to be kept for some time, it is well to put the gas under slight pressure, by opening C, whilst the reservoir is on the shelf, after the sample has been collected. A similar form of sampler has been described by Kent Smith and Towers.[1]

Apparatus for Gas Analysis

The apparatus for carrying out the analysis of gases may be divided into two groups :—

1. Apparatus in which the measuring tube serves also for the absorption.
2. Apparatus in which the measuring tube is apart from the absorption apparatus.

The first group includes the Bunsen[2] eudiometer, and the gas burettes designed by Winkler, Bunté, and Honigmann. Of these the eudiometer is not employed in technical gas analysis.

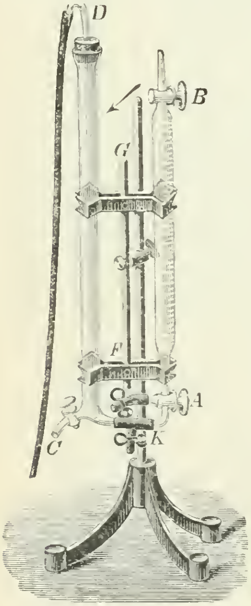

Fig. 73.

Winkler's Gas Burette.[3]—This form of apparatus is one of the earliest forms devised for technical gas analysis; although still used, it has been largely replaced by later and more convenient forms of apparatus. It consists of two communicating tubes (Fig. 73), held in position by clamps and connected at the bottom by a rubber T-piece K, the free end of which is closed by a pinch-cock, and which is made use of for cleaning out the apparatus. The graduated measuring tube is provided with a simple tap B at the top, and a three-way tap A at the bottom; the capacity between the two taps, which must be determined by an exact measurement, is about 100 c.c. The pressure tube is provided with a tap C for levelling purposes, and is closed at the top by a rubber cork D, to which a rubber tube is attached. The stand is provided with a movable holder for the tubes, so that they can be placed either in a horizontal or in a vertical position. In the manipulation of the apparatus, the measuring tube is first filled with the sample of

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[1] *J. Soc. Chem. Ind.*, 1897, **16**, 400.

[2] *Gasometrische Methoden*, R. Bunsen, 2nd edition, 1877; English translation by Sir H. E. Roscoe of 1st edition, 1857.

[3] *J. prakt. Chem.*, 1872, **6**, 303.

gas, either by suction, or by pressure, through the tap A, the tap B being kept open during the filling; after the contained air has been completely displaced, the taps are closed and the sample of gas brought under atmospheric pressure by momentarily opening A or B. The absorption liquid is then introduced into the pressure tube, and any gas below the tap A driven out, by making the connection between A and the outside air; the tap is then turned into the position connecting the two tubes. The liquid at once begins to enter the measuring tube, and its access may be facilitated by blowing through the rubber tube attached to D; after sufficient liquid has been introduced, the tap A is turned and the absorption hastened by alternately placing the tube vertically and horizontally. When no more absorption occurs the level of the liquid in the two tubes is adjusted, either by means of the tap C or of the pinch-cock at K, and the reading taken. Carbon dioxide is absorbed by potassium hydroxide, oxygen by alkaline pyrogallol, and carbon monoxide by cuprous chloride solution. Winkler[1] recommends an ammoniacal cuprous chloride solution, whilst others prefer a hydrochloric acid solution; both are reliable if a fresh solution is used for each determination, but this is necessary, as old solutions are apt to give off carbon monoxide, and may thus cause an increase of volume after absorption (*cf.* p. 210).

Bunté's Gas Burette.[2]—This burette is a development of a simpler form of apparatus due to Raoult.[3]

It consists (Fig. 74) of a burette A provided with taps *a* and *b*, of which *b* is a three-way cock; the burette is fitted with a water-jacket to protect it against rapid changes of temperature. The space between the taps is rather more than 100 c.c., and is divided into fifths of a c.c. The 100 c.c. division coincides with the bottom of the tap *b*, and the zero is 6 or 8 c.m. above the lower tap *a*; the divisions are marked for 10 c.c. below the zero. The funnel *c* is provided with a mark, and all measurements are made at atmospheric pressure, plus the pressure of a column of water, contained up to this mark in the funnel. The reservoir C, which can be attached by a rubber tube to the bottom of the burette, as shown, serves to fill the latter with water; an ordinary funnel may be used for the same purpose.

The sample of gas to be analysed is introduced by first filling the burette with water from the reservoir C; the taps *a* and *b* are then closed and the rubber tube from C detached. The three-way tap *b* is then connected with the gas supply, and the sample drawn into the burette by running water out of the bottom tap *a*. Rather more than 100 c.c. of the gas are drawn into the burette, and the adjustment to the zero mark is then made by means of the aspirating bottle S, which

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[1] *Z. anal. Chem.*, 1889, **28**, 269.

[2] *Dingl. polyt. J.*, 1878, **228**, 529.

[3] *Comptes rend.*, 1876, **82**, 844.

serves for forcing water into the burette, or for withdrawing it therefrom. In both cases the rubber tube *s* is filled with water by blowing at *t*, so as to remove all air, and whilst the water is still running out, it is attached to the tip of the burette at *a*. For the adjustment, the gas in the burette is compressed to about 95 c.c. by forcing water in from the bottle S. The tap *a* is then closed, *s* detached, and the water cautiously run out, through *a*, exactly to the zero mark. The gas is now under excess pressure, which is corrected by filling the funnel *c* up to the mark with water, and then momentarily opening the tap *b*, when the excess of gas escapes through the water. The burette now contains exactly 100 c.c. of gas at the atmospheric pressure, plus the pressure of the column in the funnel *c*. In case the burette is filled by drawing the sample of gas through it, with an aspirator, until all the air has been expelled, the adjustment is made by compressing the contained gas, by attaching the vessel C to the burette, and then adjusting as above.

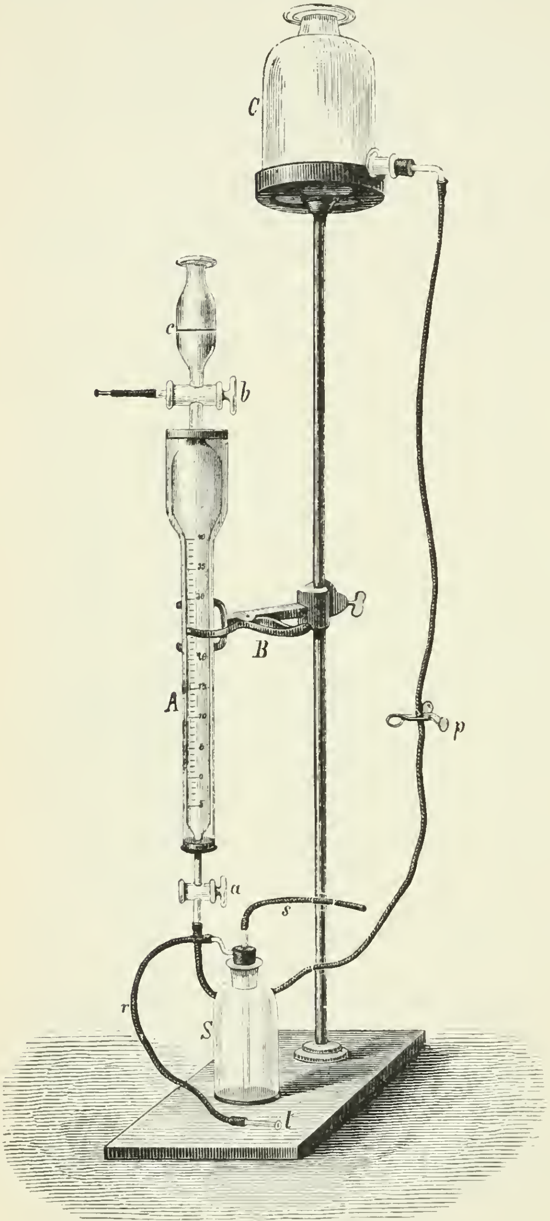

Fig. 74.

In order to absorb any one of the constituents of the gas, the absorbing liquid is introduced into the burette. This is effected by first drawing off the water below the zero mark by means of S, the rubber tube of which, *s*, is attached to the burette, after first filling it with water, as described. The tap *a* is then opened, and by applying suction at *t*, the water is readily withdrawn to a point a little above the stopcock. The suction bottle is then disconnected, the burette removed from the clamp, and the end inserted in a cup containing the absorption liquid, when on opening *a* the liquid at once rises into the burette. The tap is then closed and the contents of the burette well shaken, to facilitate the absorption of the gas. A further quantity of liquid is then admitted as before, and this is repeated, the burette being shaken after each absorption, until the level of the liquid in the burette remains constant. The pressure is adjusted by filling the funnel *c* with water and opening the tap *b*, when a little water will enter the burette; the adjustment for pressure is completed by filling *c* to the mark with water and then closing *b*, when the reading can be taken.

Owing to the adhesion of the absorption liquids to the walls of the burette, it is preferable to replace them by water, before the final readings are taken. This may be effected by removing the absorption liquid by means of the suction flask, and replacing it by water, introduced through the funnel *c*; by repeating this two or three times, the liquid is completely replaced by water. Another method is to wash out the burette by a steady stream of water, introduced through the funnel *c*, and run out through *a*, the two taps *a* and *b* being opened during the washing; when the absorption liquid has been fully removed, the pressure is adjusted as before, and the reading taken. Further absorptions are effected successively by suitable absorbents. Carbon dioxide is absorbed by potassium hydroxide, oxygen by alkaline pyrogallol, and carbon monoxide by ammoniacal cuprous chloride. The composition of the solutions employed is given on pp. 209-210.

After each analysis the burette should be thoroughly cleaned, as otherwise errors are likely to arise, especially in the determination of carbon dioxide, which may be either absorbed or produced by dirt present in the burette.[1]

A further description of the Bunté burette and of its application to the analysis of illuminating gas is given under the section "Gas Manufacture," Vol. II.

Honigmann's Gas Burette.—This burette, which is of a very simple character, is especially intended for the estimation of carbon dioxide in the carbonating gases of the ammonia-soda process. It consists of a measuring tube A (Fig. 75), of 100 c.c. capacity, closed at the top by the tap *a*, and open at the bottom, where a stout rubber tube is attached at *b*. The absorbing liquid is contained in the cylinder C. The sample

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[1] *Cf.* F. Fischer, *Z. angew. Chem.*, 1890, 3, 599; Foster and Haldane, *The Examination of Mine Air* (1905), p. 98.

of gas is introduced by an aspirator, through *a*, and after all air in the burette has been thus expelled, the tap is closed and the burette immersed to the zero mark in C, which is filled with a solution of potassium hydroxide; the tap *a* is then opened momentarily, and thus exactly 100 c.c. of gas, at the atmospheric pressure, are obtained for the absorption. This is effected by first immersing the burette somewhat lower in the solution, so as to wet the sides with the absorbent, and then drawing it out, so that the bottom of the rubber tube remains in the solution, whilst the burette is raised over the edge of the cylinder. The potassium hydroxide at once begins to enter the burette, and by agitating a few times the absorption is rapidly completed. The burette is then placed in the liquid, so that the inner and outer levels are the same, and the reading taken. The method is not to be regarded as one of great accuracy, but it is extremely simple and quick.

Fig. 75.

APPARATUS IN WHICH THE MEASURING TUBE IS APART FROM THE ABSORPTION APPARATUS.

The forms of apparatus included in this group combine both greater rapidity and more convenience in working than those described above. The earliest gas-analysis apparatus of this type was devised by Regnault and Reiset[1] (1849); it has been succeeded by a very great variety of improved forms, of which those due to Orsat, Hempel, F. Fischer, and Sodeau will be described in this section.

Of other forms used in technical gas analysis, those of Pfeiffer, Jäger, and Drehschmidt are described in connection with the analysis of illuminating gas (Vol. II.).

Orsat's apparatus.—This form of apparatus is primarily due to Schlösing and Rolland;[2] it has been modified and improved by Orsat,[3] Salleron, F. Fischer,[4] Lunge, Sodeau, and others, and is generally known as the Orsat gas analysis apparatus.

Fischer's modification consists of a measuring tube or burette A (Fig. 76), surrounded by a water-jacket, which is attached at the top to absorption vessels, generally called pipettes, D and E, by means of capillary tubes, and at the bottom to a pressure bottle L. The whole is fixed, by suitable supports, in a case, which can be closed by sliding shutters for transport. The burette has a capacity of 100 c.c., the lower portion being graduated in tenths and the upper in whole c.c. The capillary tube, leading to the pipettes, is provided with a tap at each

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[1] *J. Chem. Soc.*, 1853, 6, 128.

[2] *Ann. Chim. Phys.*, 1868, 14 [iv.], 55.

[3] *Annal. des Mines*, 1875, 8 [vii.], 485 and 501.

[4] *Fischer's Jahresber.*, 1880, 26, 330.

junction, as shown, and there is a mark *m*, on each of these, below the tap; the tap *c* is a three-way stopcock which allows of connection between the gas supply and the tube B, or between B and A, or between A and the outside air. The U-tube B is filled with cotton wool, which serves to retain any soot or dust from the gas sample. The pipettes are filled with bundles of glass tubes, so as to provide a large surface for contact, between the gas and the absorbent; the open end of each pipette is closed by a rubber stopper carrying a glass tube, to which a thin rubber ball is attached, the object of which is to protect the contained liquids from contact with the air. To prepare the apparatus for use, the pressure bottle L is filled with water and then raised, so as to drive out the air in A, through the tap *c*. The pipette D is then filled with potassium hydroxide solution, for the absorption of carbon dioxide, and the pipette E with pyrogallol solution, for the absorption of oxygen; a third pipette, charged with cuprous chloride solution, can be employed for the absorption of carbon monoxide. The method of preparing these solutions is given on pp. 209-210, in connection with Hempel's gas-analysis apparatus. To introduce the absorbing liquids, they are poured in from the back, so as to fill about half of the pipette, and then drawn up to the mark *m*, by opening the respective tap and lowering the pressure bottle L; when the liquid reaches the mark, the tap is closed and the rubber ball inserted at the back of the pipette. Before proceeding with an analysis, the apparatus should first be tested, to see whether it is air-tight. This is done by filling the burette with water, then closing the tap *c* and lowering the pressure bottle, when it will at once be seen, from any change in level of the water in A, whether there is any leak.

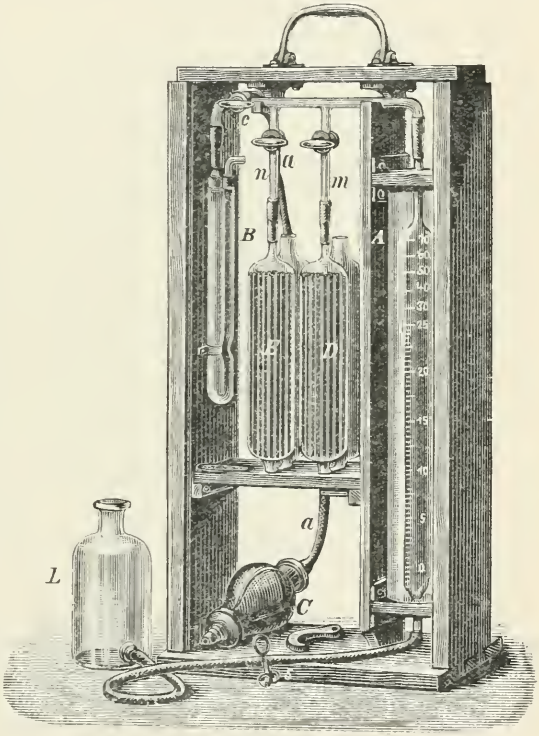

Fig. 76.

To introduce the sample of gas, A is again filled with water, the tap *c* turned, so as to communicate with B and the outside air, and the rubber aspirator C, which is connected with the gas supply, then attached to the exit tube of B; after clearing out the air in B, by aspirating, the tap *c* is turned, so as to connect the gas supply with the burette, and the sample introduced by lowering the pressure bottle L. A little more than 100 c.c. of gas are syphoned into A, and the tap *c* then closed. To obtain exactly 100 c.c. for analysis, the gas is compressed to the zero mark by raising L, the rubber tube *s*, then closed, either by the pinch-cock or by the fingers, and the tap *c* momentarily opened to the outside air, so as to establish the atmospheric pressure on the contained gas.

To determine the carbon dioxide, the tap connected with D is opened and the gas in A transferred into the pipette, by raising the pressure bottle; this operation is repeated several times, by alternately lowering and raising L, until the absorption is complete, the level of the liquid in D being finally adjusted to the mark *m*, the attached tap closed, and the reading in the burette taken, the pressure on the gas being adjusted to that of the atmosphere by raising L, so that the height of the contained liquid and that in the burette is the same. The reading obtained gives the percentage of carbon dioxide directly. The determination of the oxygen is similarly effected in the pipette E. In respect to the subsequent determination of carbon monoxide, it is to be observed that cuprous chloride solution becomes unreliable after having been used for a short time (p. 210), and Fischer prefers to omit this determination in the analysis of furnace gases. Other forms of apparatus are, of course, available for the determination of this gas, and, as already pointed out (p. 190), its quantity can also be approximately gauged from the percentage of carbon dioxide and oxygen contained in gases of this character. Carbon monoxide does not occur nearly so frequently in furnace gases, in presence of free oxygen, as has been assumed to be the case, an assumption that is largely the result of inaccurate analyses.

When the analysis is completed, the residual gas is cleared out of the burette and the apparatus is then again ready for use; an analysis can be completed in five minutes, with an accuracy of 0·2 per cent. To re-charge the pipettes, when exhausted, the contents are removed by means of a small syphon, and thoroughly washed out with water, before introducing the fresh reagent. In case any of the absorption liquid should have got into the capillary tube, above the stopcocks of the pipettes, the tubes should be thoroughly washed out with water through the tap *c*, and the water in the burette and pressure bottle renewed. It is important to grease all the stopcocks carefully before the apparatus is put aside after use.

As the result of experience with more than four thousand analyses, Fischer regards this form of apparatus as the most suitable for the examination of the gases from boiler furnaces,[1] heating apparatus, brick kilns, pottery kilns, ultramarine kilns, black-ash furnaces,[2] and the like, and also as advantageous for the examination of blast-furnace gases, cupola-furnace gases,[3] the gases from puddling furnaces,[4] the saturation gases in the manufacture of sugar, and for the study of petroleum lamps and of gas engines.[5]

Lunge's modification[6] **of the Orsat apparatus** (Fig. 77) is arranged for the determination of hydrogen, in addition to that of carbon dioxide, oxygen, and carbon monoxide. The pipettes *b*, *c*, *d*, are provided for the absorption of the latter gases, and are charged with potassium hydroxide, alkaline pyrogallol, and cuprous chloride respectively; the

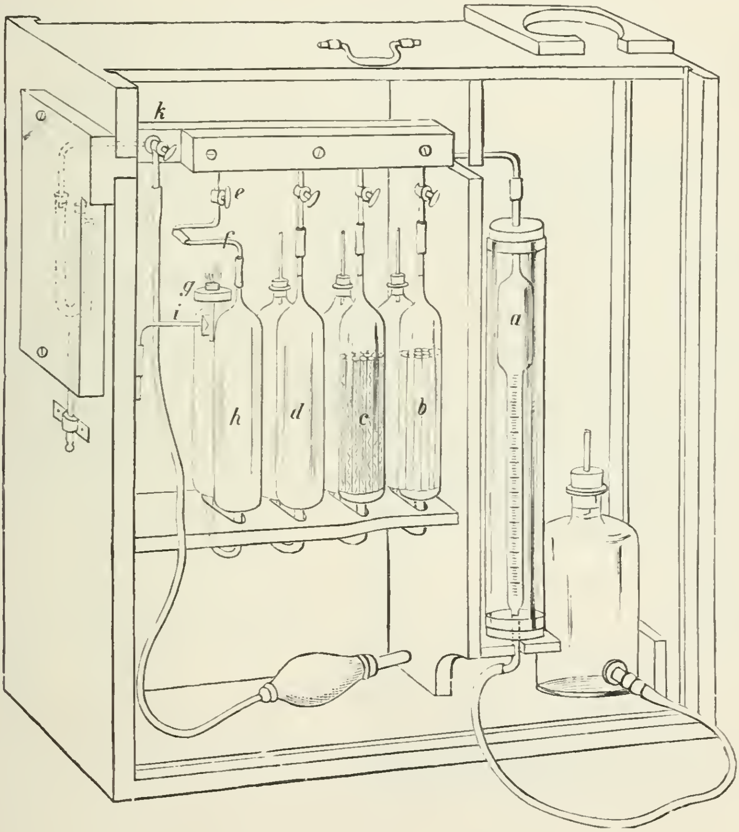

Fig. 77.

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[1] *Dingl. polyt. J.*, 1878, **229**, 130; 1879, **232**, 346; **233**, 183. *Fischer's Jahresber.*, 1881, **27**, 146, 1045 and 1050; 1882, **28**, 131; 1883, **29**, 1289; 1885, **31**, 1295.

[2] *Fischer's Jahresber.*, 1878, **24**, 431; 1880, **26**, 274; 1881, **27**, 35 and 1047.

[3] *Ibid.*, 1879, **25**, 71; 1884, **30**, 37; 1885, **31**, 37.

[4] *Ibid.*, 1881, **27**, 35.

[5] *Ibid.*, 1883, **29**, 1229.

[6] *Dingl. polyt. J.*, 1882, **245**, 512.

manipulation of the apparatus is in every way similar to that of the Orsat-Fischer form. The determination of hydrogen is effected by combustion over a palladium asbestos fibre, placed in the capillary tube *f*; the tube is connected to the pipette *h*, which is filled with water, and through the tap *e*, to the capillary connecting tube of the apparatus. The small spirit lamp *g*, carried by the movable rod *i*, is for heating the palladium asbestos. To carry out the combustion, the residual gas, after the absorption of the carbon dioxide, oxygen, and carbon monoxide, is first mixed with air in the burette *a*; this is admitted through the tap *k*, by lowering the pressure bottle, and sufficient air is added to bring the total volume up to about 100 c.c. If the gas is very rich in hydrogen, it is advisable, either to add a further proportion of air after the first combustion has been completed, or to repeat the combustion with the residual mixture, or to substitute oxygen for air in the first instance. The reading of the total volume of gas and air (or oxygen) is first taken, and the mixture passed through the tap *e*, over the palladium asbestos, previously gently heated; the temperature of the tube should be such as to allow of its being touched, for a moment, without burning the fingers. The progress of the combustion is at once indicated by the glowing of the asbestos thread at the end where the gas enters, and by carefully syphoning the mixture backwards and forwards several times, complete combustion is effected; this is checked by the volume remaining constant. If carbon monoxide is combusted with the hydrogen, the residual gas must be passed into the pipette *b*, to remove the carbon dioxide formed, and the total contraction measured after this absorption.

Example of Analysis.

100 *c.c. of Generator Gas gave the following readings on the burette*:—

1. *After absorption of Carbon dioxide*	3·2
2. *After absorption of Oxygen*	3·2
3. *After absorption of Carbon monoxide*	24·2
4. *After addition of Air*	0·9
5. *After combustion*	10·8
6. *After absorption of Carbon dioxide formed in* 5	11·4

The percentage volumes of carbon dioxide and oxygen are obtained directly from the above data. The total contraction is $11{\cdot}4 - 0{\cdot}9 = 10{\cdot}5$; of this $11{\cdot}4 - 10{\cdot}8 = 0{\cdot}6$ is due to the formation of carbon dioxide, and since carbon monoxide forms its own volume of carbon dioxide, on combustion, this represents the volume of carbon monoxide present and not previously absorbed by the cuprous chloride solution. The total carbon monoxide is, therefore, $24{\cdot}2 - 3{\cdot}2 + 0{\cdot}6 = 21{\cdot}6$. Since both 2 volumes of hydrogen and 2 volumes of carbon monoxide require 1 volume of oxygen for combustion, two-thirds of the total contraction represents the hydrogen and unabsorbed carbon monoxide, and by subtracting the latter, the volume of hydrogen present is obtained—$(11{\cdot}4-0{\cdot}9\times\frac{2}{3})-0{\cdot}6=6{\cdot}4$. The composition of the gas is therefore:

Carbon dioxide	3·2
Oxygen	0·0
Carbon monoxide	21·6
Hydrogen	6·4
Nitrogen and some Methane	68·8
	100·0

W. H. Sodeau's modification[1] **of the Orsat apparatus** is designed for the analysis of mixtures containing small proportions of combustible gases, and is especially applicable to the examination of chimney gases. It can be readily used in the stokehold, and in combination with a suitable high temperature thermometer it affords a ready means of determining the total chimney losses, including those due to unburnt hydrogen, which are usually ignored; the efficiency of boilers can thus be ascertained. The distinguishing feature from the ordinary Orsat, is the replacement of the cuprous chloride pipette and palladium combustion tube, by an adaptation of the Winkler combustion pipette (p. 214). The apparatus is shown in Fig. 78.

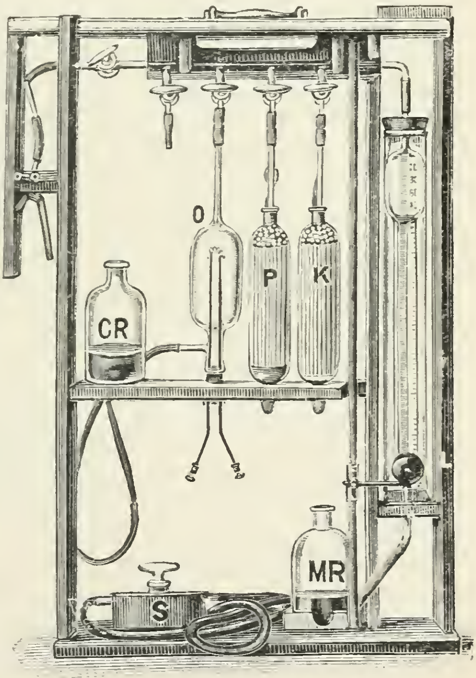

Fig. 78.

The combustion pipette may consist of two separate vessels, the combustion bulb O and the aspirator CR, as shown in the figure, or it may be shaped somewhat like an ordinary Hempel pipette for solid absorbents (Fig. 84, p. 206), provided with a straight instead of with a bent capillary tube. The bulb O is provided with a spiral of platinum wire 0·25 to 0·3 mm. in diameter, attached to a pair of unlacquered brass electrodes, and is heated by a current of about 5 amperes, obtained either by means of a 4-volt accum-

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[1] *Chem. News*, 1904, **89**, 61; Eng. Pat. 12225, 1906. The editor is indebted to Dr W. H. Sodeau for this description of his apparatus; it is made by Messrs Brady & Martin, Newcastle-on-Tyne.

ulator, using a short length of iron wire as a controlling resistance, or from a lighting circuit, connected through a few lamps in parallel; water is used as the confining liquid. A lens L, mounted on a fitting which slides on a vertical rod, gives increased accuracy in reading, owing to the elimination of errors of parallax. The pipettes K and P are for the determination of carbon dioxide and of oxygen respectively.

Analysis of chimney gas. After determining the carbon dioxide, as usual, by means of the potash pipette K, the gas is passed into the combustion pipette and the current turned on for one to two minutes, when the gas is syphoned back and the contraction measured. The carbon dioxide produced by the combustion is then determined by a one-minute absorption in the pipette K; the decrease in volume gives the percentage of carbon monoxide. Half the volume of the carbon dioxide produced represents the contraction due to the combustion of the carbon monoxide; this value is deducted from the total contraction on combustion, and two-thirds of the difference equals the percentage of hydrogen present. Only one absorbent is thus required for the analysis. The determination of these three constituents can be completed within fifteen minutes, and by means of appropriate curves the results can be stated as lbs. of air used per lb. of fuel, and loss of heat as unburnt gases, provided the composition of the fuel is approximately known. For ordinary practical purposes, the determination of oxygen is, therefore, unnecessary. It may, however, be carried out by means of the pyrogallol (or phosphorus) pipette P, either after the other constituents have been determined, in which case the amount consumed in the combustion is added, or else immediately after the first determination of carbon dioxide, in which case it is necessary to draw in a little air and to re-measure the total volume before combustion.

Rapid joint estimation of carbon monoxide and hydrogen. As these two gases are, volume for volume, of nearly identical calorific value, it often suffices to make a joint determination of the two, after absorption of the carbon dioxide. For this purpose it is necessary to employ a combustion pipette with a movable reservoir, CR, as shown in Fig. 78. The measurement after combustion is omitted, in order to save a little time. The large stopcock S is closed as soon as the gas has been driven over into the combustion pipette O. After combustion, the tap of the potash pipette K is opened, and the gas directly transferred, by raising CR and finally closing the tap of O; after allowing one minute for absorption, the stopcock S is opened, the residue drawn back into the measuring tube, and the tap of K closed. Two-thirds of the contraction equals the percentage of "combustible gases," *i.e.*, carbon monoxide and hydrogen.

A simpler and more compact form of this apparatus is also made which is specially suitable for the work of marine engineers.

A modified Orsat apparatus, specially designed for the analysis of generator gas, has been devised by Meyer.[1] The measuring burette has a capacity of 120 c.c., and a platinum spiral combustion pipette is provided.

Hempel's Apparatus. — This is, in part, a development of the Ettling gas pipette; it is a much used and very adaptable form of apparatus.

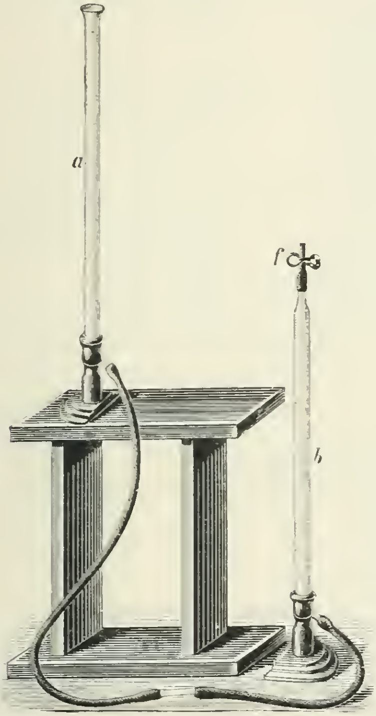

Fig. 79.

Fig. 81.

The burette (Fig. 79), consists of a measuring tube *b*, graduated into 100 c.c. with 0·2 c.c. divisions, and the pressure tube *a*, each of which is contracted at the lower end and bent at right angles, so as to fit into slots in weighted wooden supports. The measuring tube is also contracted at the top, and terminates in a capillary tube $\frac{1}{2}$ to 1 mm. in diameter and 3 cm. long. The tubes are connected by a piece of rubber tubing about 100 cm.

Fig. 80.

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[1] *Z. angew. Chem.* 1905, 18, 446.

in length, which is preferably divided in the middle, and the parts joined together by a short piece of glass tubing, to facilitate the cleaning of the burette.

A short piece of thick-walled rubber tubing, provided with a pinch-cock, is attached at *f*.

A modified form of burette, which has many advantages in practice, has the rubber connection and pinch-cock at *f* replaced by a three-way tap, of the form shown in Fig. 80.

Another modification, generally known as the modified *Winkler burette*, is shown in Fig. 81. This is provided with a simple gas tap at *a* and with a three-way tap at *b*; its chief advantage is in the analysis of mixtures containing an easily soluble gas, since the initial volume of gas can be measured without bringing it into contact with water, which is always used as the confining liquid in the various forms of Hempel burette employed for technical analysis.

Any of these forms of burette may be provided with a water-jacket, if desired, in order to minimise the errors due to changes of temperature.

The pipettes, in which the various reagents for the absorption of the gases are contained, consist of two bulbs, *a* and *b* (Fig. 82), connected by the tube *d*, of which *b* is attached to a capillary tube *c* of $\frac{1}{2}$ to 1 mm. diameter; a white porcelain plate *m*, is fixed at the back of *c*, to render the thread of liquid in the capillary more visible. The capacity of the bulb *b* is about 150 c.c., that of *a* about 100 c.c.; this allows of a sufficient quantity of the absorbent being left in *b*, after the introduction of 100 c.c. of gas. The pipettes are mounted either on wooden (Figs. 82 and 86) or on adjustable iron frames (Figs. 83, 84, 85, and 87). Pipettes for use with solid absorbents, such as phosphorus, are provided with a cylindrical bulb, tubulated at the bottom (Fig. 84), and are closed by a good rubber stopper; double pipettes (Figs. 85 and 86) are used

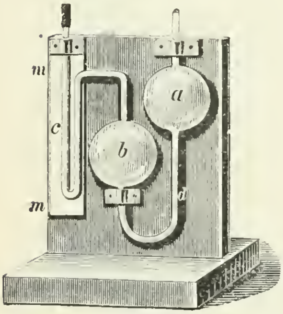

FIG. 82.

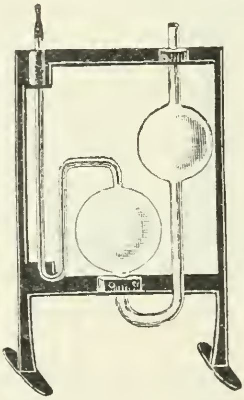

FIG. 83.

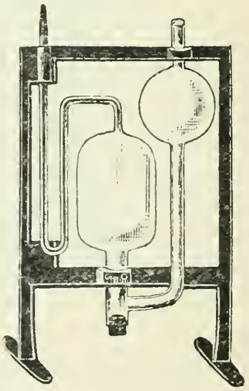

FIG. 84.

for absorbents which require to be protected from the air, such as pyrogallol, or which evolve irritating fumes, such as bromine.

A good form of simple pipette, in which a small second bulb, filled with glass beads, is placed above the absorption bulb, is shown in Fig. 87.

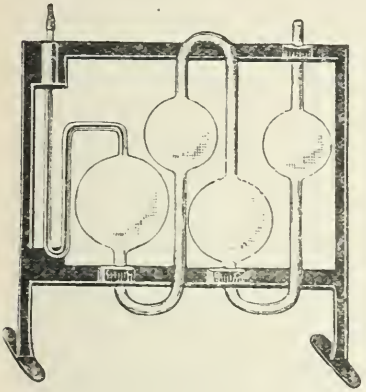

Fig. 85.

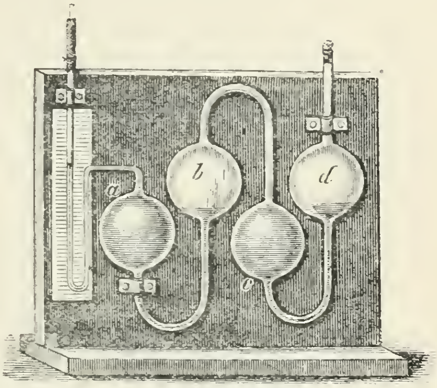

Fig. 86.

The simple pipettes are filled by pouring the absorbent through the tube attached to the bulb *a* (Fig. 82), whilst the air is sucked out from *b*; sufficient of the liquid is introduced to entirely fill the bulb *b*, the capillary tube *c*, and to leave a small quantity in *a*. To fill the double pipettes, the best plan is to attach a glass tube a metre long, and provided with a funnel, to the top of the capillary tube, and to pour the absorbent liquid in through this, until the first bulb is completely filled; to effect this, without the liquid overflowing to the protecting bulbs *c* and *d* (Fig. 86), it is necessary to blow out the air contained in *a* through the funnel, several times successively, after a portion of the absorbent has been introduced. After *a* and the lower part of *b* have been filled, water is introduced into *d* and *c*, through the tube attached to *d*, after first blowing over a portion of the liquid in *a* into *b*, so as to remove the air in the latter.

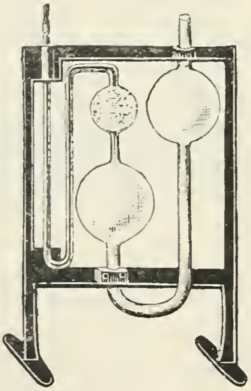

Fig. 87.

The burette and pipettes are connected by a piece of thick-walled capillary tubing of 1 mm. internal diameter and 18 cm. in length, as shown in Fig. 88, the attachment to the pipette and burette being made by means of stout rubber tubing.

To introduce gas, for analysis, into the burette, the pressure tube B (Fig. 88) is filled with water and then raised, so as to completely drive out the air in the measuring tube A, and the pinch-cock or tap at *f* closed; the gas supply is then attached at *f*, and the sample syphoned in, by opening *f* and lowering the pressure tube. A little more than 100 c.c. of gas are drawn in and then *f* is closed When the Winkler modification of the burette (Fig. 81) is used for the analysis of a mixture containing a very soluble constituent, the sample is introduced through the three-way tap *b*, at the bottom of the burette. To obtain exactly 100 c.c. of gas for analysis, the pressure tube is raised gradually and the connecting rubber tube closed, by pressing it between the thumb and finger, when the liquid stands exactly at the 100 c.c. graduation; *f* is then momentarily opened to establish the atmospheric pressure, and the volume verified by bringing the water in the two tubes of the burette to the same level.

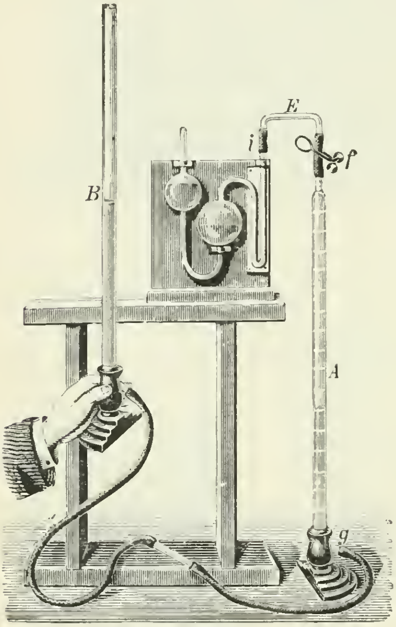

Fig. 88.

The burette and the pipette are then connected, as shown in Fig. 88. To obviate the error due to the air in the capillary tube E, it is first connected to the pipette, and the absorbent liquid blown over from the latter until it begins to run out at the free end of the capillary, when it is at once attached to the burette; it is convenient to attach a piece of rubber tubing to the tube of the upper bulb of the pipette for this purpose. The transference of the gas, from the burette to the pipette, is effected by raising the pressure tube and opening *f*; sufficient water is driven over to wash out the capillary tube of the pipette, as far as the top of the absorption bulb, so that the gas is confined between two surfaces of liquid, and *f* is then closed. The absorption, is promoted by gently shaking the burette; some recommend the removal of the capillary E for this purpose, but sufficient movement can be given to the liquid without disconnecting. After absorption, the gas is syphoned back into the burette by lowering B, the liquid in the pipette being drawn over as far as the pinch-cock (or stopcock) at *f*; after allowing two minutes for the water in the burette to drain, the liquid in the two tubes of the burette are brought to the same level and the reading taken. The absorption is repeated until a constant value is obtained, and the decrease in volume, with each reagent, represents the percentage of absorbed gas present in the mixture. The capillary connecting tube E must be thoroughly cleaned after each successive reagent.

As the Hempel apparatus is not used for work of high accuracy, some workers prefer to avoid introducing the absorbents into the connecting capillary tube, and in transferring the gas from the burette to the absorption pipette, and in syphoning it back, only bring the confining liquid as far as the tap of the burette and the top of the capillary of the pipette respectively.

The Hempel apparatus can be used for the analysis of mixtures containing carbon dioxide, oxygen, carbon monoxide, hydrogen, methane, nitrogen, olefines, and hydrocarbon vapours. The methods adopted for the determination of the two latter will be described in connection with the analysis of illuminating gas (Vol. II.); the other gases are determined in the order given, either by absorption or by combustion.

Carbon dioxide. A solution of potassium hydroxide, containing one part potassium hydroxide to two parts water, is used for the absorption.

Oxygen. Either alkaline pyrogallol or phosphorus is used as the absorbent. The pyrogallol solution is made up by dissolving 20 g. of pyrogallol in 500 c.c. of potassium hydroxide solution (1 : 2); this large excess of alkali is necessary, as otherwise an appreciable quantity of carbon monoxide may be formed, when gases rich in oxygen are passed into pyrogallol.[1] A double pipette (Figs. 85 and 86) is used with this reagent.

Phosphorus is a very energetic absorbent for oxygen, but its action is hindered by even traces of certain gases and vapours, such as the unsaturated hydrocarbons, phosphoretted hydrogen, ammonia, and alcohol vapour; also the absorption is very slow below 14°. This reagent is used in the form of thin rods, surrounded by water, in the pipette for solid absorbents, shown in Fig. 84. As phosphorous oxide fumes are evolved in the absorption, these are removed by passing the gas into a potassium hydroxide pipette, after the absorption of oxygen is complete. The water in the pipette should be renewed, from time to time, as it becomes saturated with phosphorous acid, and the pipette should be kept in the dark, when not in use, to avoid the formation of the inactive amorphous phosphorus.

Sodium hydrosulphite has also been proposed as an absorbent for oxygen;[2] it is cheaper than pyrogallol, and absorbs oxygen equally readily, at low and at higher temperatures. The solution is prepared by dissolving 50 g. of the salt in 250 c.c. of water and adding 40 c.c. of a sodium hydroxide solution, containing 500 g. of alkali to 700 c.c. of

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[1] *Cf.* Hempel, *Ber.*, 1885, **18**, 278; Clowes, *J. Soc. Chem. Ind.*, 1896, **15**, 170.

[2] *Cf.* H. Franzen, *Ber.*, 1906, **39**, 2069.

water, and is used in a pipette filled with rolls of iron-wire gauze; the absorption takes place according to the equation:

$$Na_2S_2O_4 + H_2O + O = 2\ NaHSO_3.$$

Carbon monoxide. Cuprous chloride, either in ammoniacal or in hydrochloric acid solution, is used as the absorbent, and double pipettes must be employed. The former solution is prepared by dissolving 10 g. commercial cuprous chloride in 250 c.c. hydrochloric acid (concentrated), and reducing the cupric chloride present, by the addition of copper gauze, until the solution is colourless; the acid liquid is then poured into 1500 c.c. of water, the water decanted, after allowing to stand for twenty-four hours, and the cuprous chloride dissolved in 250 c.c. ammonium hydroxide of sp. gr. 0·91. Another method is to prepare a stock solution, by dissolving 200 g. of cuprous chloride in a solution of 250 g. of ammonium chloride in 750 c.c. of water; this solution must be kept in stoppered bottles and made up for use as required, by the addition of one-third of its volume of ammonium hydroxide of sp. gr. 0·905. The hydrochloric acid solution is prepared as above, by dissolving commercial cuprous chloride in hydrochloric acid, in presence of copper gauze. Sodeau recommends dissolving 100 g. cupric chloride (cryst.) in 500 c.c. hydrochloric acid (conc.) and 500 c.c. water, and placing this solution in a number of small narrow-mouthed bottles, of about 150 capacity, containing rolls of copper gauze; the reagent is ready for use as soon as it has become colourless, and the bottles are filled up each time that a portion of the contents is withdrawn. It is to be borne in mind that cuprous chloride also absorbs oxygen, ethylene, and acetylene, so that these gases must be previously removed, if present.

The absorption of carbon monoxide by cuprous chloride is much slower than that of carbon dioxide and oxygen by their respective reagents, and it has further been established by Drehschmidt[1] and by Winkler[2] that cuprous chloride solutions, after they have absorbed a considerable volume of carbon monoxide, give up a portion of the absorbed gas, when shaken with an indifferent gas, as in the ordinary course of analysis. Hence, an increase of volume, instead of a decrease, may occur after the absorption. This source of error is avoided by using two pipettes successively, the first for the absorption of the bulk of the gas and the second for the final residue; after the former is sufficiently exhausted, it is re-charged and the order of the two pipettes reversed. Drehschmidt's experiments show that the ammoniacal solution of cuprous chloride is preferable to the hydrochloric acid solution, in respect to the liberation of absorbed carbon monoxide.

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[1] *Ber.*, 1887, **20**, 2572; 1888, **21**, 2158.

[2] *Z. anal. Chem.*, 1889, **28**, 269; *J. Soc. Chem. Ind.*, 1889, **8**, 570.

Hydrogen. This gas is practically always determined by combustion with oxygen, either over palladium asbestos or by explosion. The former method is carried out by replacing the connecting capillary tube E (Fig 88), by a similar tube containing a thread of asbestos fibre, coated with metallic palladium, which is heated as described in connection with the Lunge-Orsat apparatus (p. 202).

To prepare the fibre, 1 g. of palladium is dissolved in aqua regia, the solution evaporated to dryness on the water-bath, and the residual chloride dissolved in a little water; the solution is then reduced by the addition of a few c.c. of a cold saturated solution of sodium formate and sufficient sodium carbonate, to render the whole strongly alkaline. About 1 g. of long-fibred, soft asbestos, which should suffice to absorb the whole of the liquid, is soaked in the solution, and the fibre dried at a gentle heat; it is then carefully washed to remove adhering salts and again dried, when it is obtained as a dark-grey coloured product, containing about 50 per cent. of metallic palladium. The capillary combustion tube is 15-16 cm. long, 1 mm. bore, and 5 mm. external diameter. To introduce the fibre, a few loose strands are moistened with water and then rolled into a fine straight thread, which is slid into the capillary tube, whilst held vertically and before it has been bent, for attachment to the burette and pipette. The thread is easily brought into position in the centre of the tube; the water is then drawn off, by means of filter paper, the moisture removed by drying, and the ends of the tube bent at right angles for a length of 3·5 to 4 cm.

The capillary tube is attached on the one side to the burette in the usual way, and on the other, to a simple pipette filled with water. To carry out the combustion, not more than 25 c.c. of the gas in the burette is first passed over into the pipette, the necessary quantity of air (about 75 c.c. should suffice) then introduced into the burette, its volume measured and also the volume of gas+air, after syphoning back the former from the pipette, as a check. The mixture is next passed into the pipette, which is gently shaken so as to mix the whole, and then passed backwards and forwards over the heated palladium asbestos till no further contraction occurs; two-thirds of this contraction is due to the hydrogen. The level of the confining liquid is brought to the bottom of the capillary combustion tube, in syphoning the gas to and from the burette. For the introduction of the air or oxygen, the burette with the three-way tap at the top (Fig. 80) is very advantageous, as it avoids disconnecting the capillary tube.

This method is very valuable as a means of determining hydrogen, in presence of methane; the latter is not combusted under the above conditions, if the temperature does not exceed 500°.[1] Carbon monoxide

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[1] *Cf.* H. G. Denham, *J. Soc. Chem. Ind.*, 1905, **24**, 1202; O. Brunck, *Z. angew. Chem.*, 1903, **16**, 695; *J. Soc. Chem. Ind.*, 1903, **22**, 925.

can be similarly determined by combustion over palladium asbestos, the carbon dioxide formed being subsequently absorbed by potassium hydroxide. The determination of hydrogen, by explosion with oxygen, is carried out in the Hempel explosion pipette (Fig. 91).

The determination of hydrogen by absorption with palladium. Hempel has worked out the conditions under which the well known power possessed by palladium of absorbing hydrogen can be made use of for the determination of the gas.

Pure palladium is indifferent towards a mixture of hydrogen, methane, and nitrogen, but if it contains a small proportion of palladious oxide, a partial combustion of the hydrogen occurs, and the heat thus generated is sufficient to ensure the absorption of the rest of the hydrogen present; the process is accordingly in part a combustion and in part an occlusion of the hydrogen.

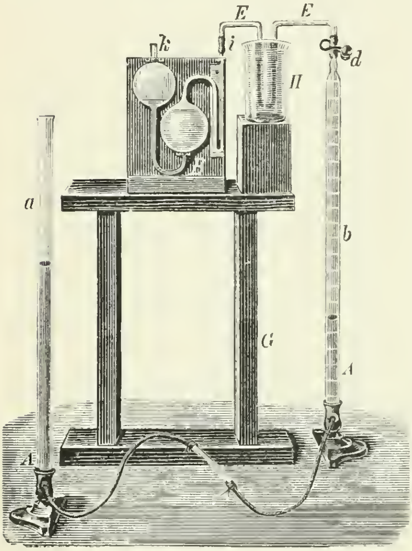

Fig. 89.

The palladium is prepared by heating 4 to 5 g. of palladium sponge, in portions of 1 g. at a time, on the lid of a platinum crucible, until it nearly glows, and then allowing it to cool slowly, whereby a thin film of oxide is formed upon the surface of the metal. For use, 4 g. of this oxidised sponge is placed in a U-tube, of 4 mm. internal diameter and 20 cm. total length; the tube is placed in a beaker, and kept at a temperature of 90° to 100° by hot water, as shown in Fig. 89.

To carry out the determination, the U-tube is attached on the one side to the burette, and on the other to a pipette charged with water, and the gas syphoned backwards and forwards three times; the beaker H is then replaced by one containing cold water, and the gas again passed twice through the tube, so as to cool it to the original temperature. The volume is finally adjusted by syphoning the liquid in the pipette to *i*, and the reading taken; the decrease in volume represents the absorbed hydrogen and the volume of oxygen originally contained in the U-tube. The latter is determined, once for all, by closing one end of the U-tube with a glass stopper attached by a piece of rubber tubing, and then placing it in a beaker of water at 9°; the open end of the tube is then connected with the burette, previously filled with water, and the tube heated in the beaker to 100°. The increase of volume, as measured in the burette, is that due to an increase of 91° in temperature, and therefore equal to one-third of the volume of gas; from this value the volume of oxygen in the U-tube is obtained. The palladium is regenerated, after use, by first passing air over it, when it gets quite hot; any drops of water that may collect are removed, the palladium then shaken out of the tube and oxidised as before.

Carbon dioxide, oxygen, and carbon monoxide, heavy hydrocarbons, and vapours of hydrochloric acid and of ammonia, prevent the determination of hydrogen by this method, and it is but seldom used in technical gas analysis. It has, however, the advantage that since no air is added, there is no restriction as to the volume of the gas that can be used for the analysis.

Methane is determined by combustion with oxygen, either by explosion or by a heated platinum wire.

The determination of methane by explosion. The Hempel explosion pipette is used for this method. The earlier form of this pipette is shown in Fig. 90; it is an ordinary simple pipette, provided with electrodes at *k* and a stopcock at *d*, and is filled with water. An improved form of pipette, in which mercury is used as the confining liquid, is shown in Fig. 91; the second bulb of the ordinary pipette is replaced by a levelling bulb, attached by a stout piece of rubber tubing. It is advantageous to have a small stopcock fitted to the top of the capillary tube at *c*, so that the mixture of gas and air or oxygen can be fired, without risk of loss by leakage.

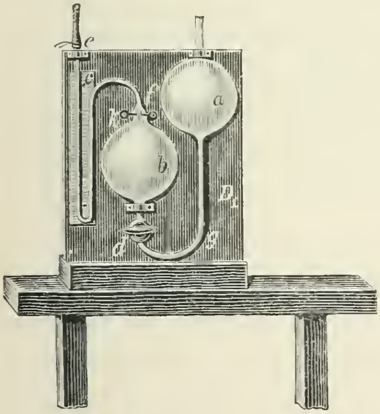

FIG. 90.

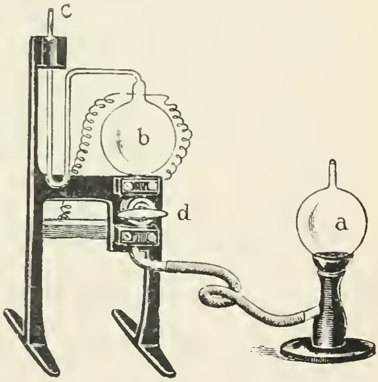

FIG. 91.

To carry out the determination, the residual gas, after the determination of the hydrogen, is syphoned over into the explosion pipette, the necessary quantity of air or oxygen added, in the same manner as in the combustion of hydrogen over palladium asbestos, the total volume then measured as a check, and the whole passed over into the pipette, where it is mixed by gentle shaking; the water in the burette is syphoned over until the capillary tube of the burette is filled, when the tap at *c* is closed. The pressure on the mixture is reduced slightly, before firing, by lowering the pressure bulb *a*; the tap *d* is then closed and the gases fired by attaching the terminals of a small Ruhmkorff coil to the electrodes of the pipette. After the combustion, the gas is syphoned back into the burette, and the carbon dioxide formed determined by absorption with potassium hydroxide.

In respect to the volume of air or oxygen to be added for the combustion, the ratio of the total combustible to incombustible gases must be between the limits of 26 to 64 : 100, in order to ensure no nitrogen being simultaneously oxidised;[1] a ratio of 50 : 100 is a good working proportion, it being borne in mind that the oxygen required theoretically for the combustion of the methane, according to the equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O,$$

is included in the combustible gases, the excess forming part of the incombustible gases. The choice of air or oxygen will accordingly be decided by the volume of the gas to be dealt with and its content of methane; oxygen from the ordinary oxygen cylinders can be conveniently used, the percentage of the contained oxygen having been previously determined. One-third of the total contraction, after the absorption of the carbon dioxide, represents the volume of methane present.

Methods for the simultaneous determination of two or three combustible gases, such as hydrogen, carbon monoxide, and methane, are described in connection with the analysis of illuminating gas (Vol. II.). The residual gas, after combustion, contains the nitrogen and the excess of air or oxygen; the nitrogen, in the original sample, is taken by difference.

Combustion of methane by a heated platinum wire. Methane is completely combusted, without explosion, by passing it, mixed with oxygen, over a heated surface of platinum. Winkler[2] designed a modified form of Hempel pipette for this purpose, in which a small platinum spiral, enclosed in the bulb of the pipette, is heated by an electric current. A much more convenient device for this method of determination is the Drehschmidt[3] capillary tube shown in Fig. 92. This consists of a seamless platinum tube, 20 cm. long, 2 mm. thick, and 0·7 mm. internal

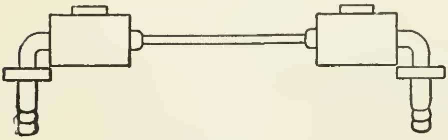

FIG. 92.

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[1] Bunsen, *Gasometrische Methoden*, 2nd edition, p. 72.

[2] *Z. Anal. Chem.*, 1889, **28**, 269; *J. Soc. Chem. Ind.*, 1889, **8**, 570.

[3] *Ber.*, 1888, **21**, 3245.

diameter, containing three or four pieces of platinum wire; pieces of brass tubing are soldered to the ends of the platinum tube, which serve for connecting to the measuring tube and pipette. Two small cooling cylinders, also made of brass, are fixed on to the brass tubes, just above the bend. The tube must be tested before use, to make sure that it is air-tight.

To carry out the combustion, the capillary tube is attached by rubber connections to the burette and to a pipette charged with potassium hydroxide, in the usual way, and the mixture of gas and air (or oxygen) obtained, as described above; the tube is then heated to a bright red heat, preferably by a flat-flamed Bunsen burner, and the gaseous mixture passed backwards and forwards twice, over the heated platinum. The reading is taken after a final absorption in the potassium hydroxide pipette, and one-third of the total contraction represents the methane present.

F. Fischer's Apparatus.[1]—In this apparatus (Fig. 93), either mercury or water is used as the confining liquid; it has been designed especially for the analysis of producer gas, "mixed" or semi-water gas, and water gas. A similar form of apparatus, of a more complex character, was previously designed by Frankland and Ward,[2] and subsequently modified by McLeod,[3] and by Thomas.[4]

The essential parts consist of the bulb or laboratory vessel A, in which the absorptions and combustions are effected, the measuring tube M, surrounded by a water-jacket, and the levelling tube D. The upper part of A must be sufficiently wide to prevent the adherence of drops of liquid; the measuring tube is graduated either in millimetres or in cubic centimetres, and must be calibrated by mercury if the former method of graduating is adopted. Pressure bulbs, F and L, supported on wooden blocks and movable in the notches of the frame H, are attached to A, and to the tube V, which is connected with the measuring and levelling tubes respectively. The combustion spiral *g* (Fig. 94) consists of a nickel tube in which a nickel wire *v*, insulated by a glass tube, is fixed, the ends of which are connected by a spiral of platinum wire; the free ends of the wire project outside the bulb A, and are attached to binding screws. In order to keep the platinum wire at the right temperature, and so prevent its becoming detached by excessive heating, an adjustable resistance should be placed in the circuit, to regulate the current; three Grove cells will keep the spiral red hot for one and a half to two minutes, which is sufficiently long for a combustion to be completed. The tubes attached to the measuring tube and the laboratory vessel are connected at *v*, by rubber tubing and brass clips (the distance between *v* and *d* is somewhat greater than

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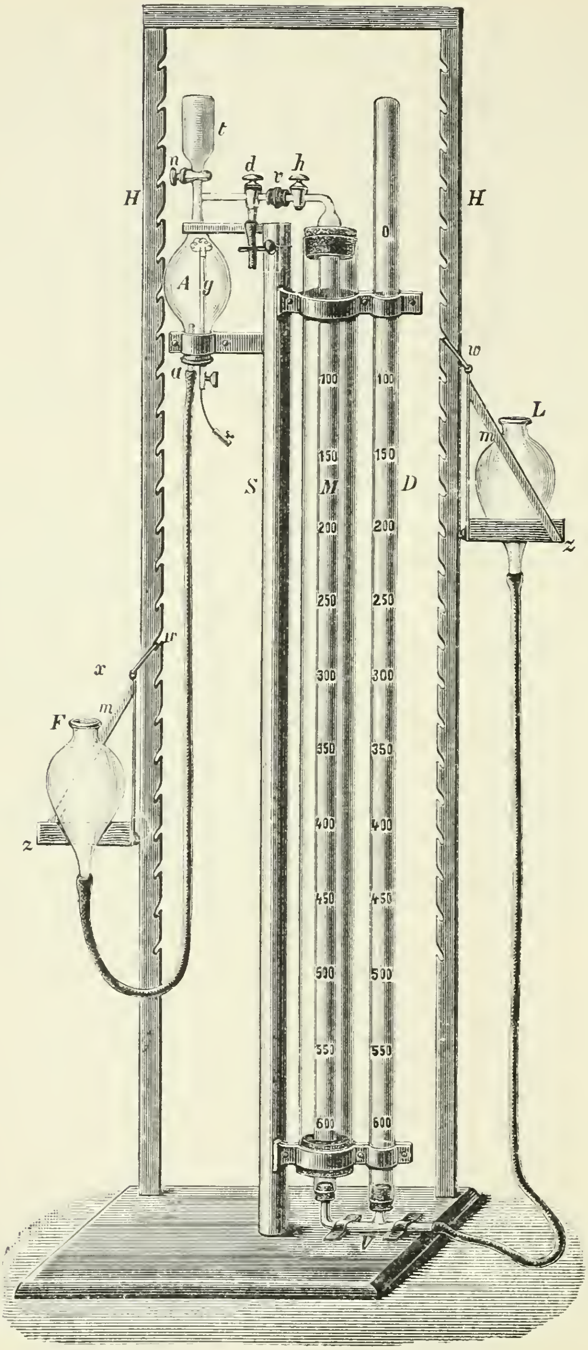
[1] *Z. angew. Chem.*, 1890, **3**, 591.

[2] *J. Chem. Soc.*, 1853, **6**, 197.

[3] *Ibid.*, 1869, **22**, 313.

[4] *Ibid.*, 1879, **35**, 213.


t
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S
M
D
w
L
m
z
x
m
F
z
V

Fig. 93.

represented in the figure); *d* and *n* are three-way taps, and *h* a simple straight-bore tap.

To introduce the gas sample, *g* is drawn down to the bottom of the laboratory vessel, and A, M, and D filled with mercury by raising F and L; the taps *d* and *h* are then closed and the gas syphoned into A, through the three-way tap *d*, by turning it so as to connect the gas-supply with the laboratory vessel. If the gas is to be drawn from a sealed bulb (Fig. 68, p. 193), this is attached to the rubber tube connected with the tap *d*, and the end broken inside the tubing; the other end is broken off under mercury, in a suitable containing vessel, and the gas drawn into A by lowering the pressure bottle F. The gas is then syphoned from A into the measuring tube, any excess being removed through *d*, by making the connection with the outside air. After reading the volume of the gas in M, 0·3 to 0·5 c.c. of potassium hydroxide solution are introduced into A, through the funnel *t*, for the absorption of carbon dioxide. The gas is then transferred from M into A, and syphoned back to a mark just in front of the tap *d*, after the absorption. The volume of the connecting capillary tube up to this mark must be ascertained, in the calibration of the measuring tube, and allowed for. For the absorption of oxygen, 0·1 c.c. of a 1 : 3 pyrogallol solution is similarly introduced into the laboratory vessel. After the determination of these gases, A must be thoroughly cleaned, before the hydrogen, carbon monoxide, and methane are combusted; this is effected by washing it out two or three times with 10-20 c.c. of water, which is introduced through the funnel *t*, and expelled through the tap *d*. If any of the absorbent has inadvertently got beyond *d*, or into the measuring tube, it is removed by first clearing the air out of A, syphoning water from the laboratory vessel into M, and then drawing back the gas and liquid into A, until the mercury reaches *d*; the gas is next syphoned back into M, and the wash-water expelled, as before, through *d*.

FIG. 94.

The combustion of the remaining gases is effected by drawing in the necessary quantity of air or oxygen, through the tap *d*, into the measuring vessel; the volume of the mixture is then measured, the tube carrying the platinum spiral pushed into position in the upper part of A (as shown in Fig. 93), the electric current turned on, and the gas transferred into A by raising the pressure bottle L. The combustion generally takes place quietly, without any explosion; at most, a slight and quite harmless explosion occurs. The gas is syphoned back, after combustion, into M, and the contraction measured; the carbon dioxide formed is determined by absorption with potassium hydroxide, as described above. Finally, the excess of oxygen can be determined by absorption with pyrogallol and the residual nitrogen measured.

The volume of air required for every 100 volumes of producer gas, semi-water gas, and water gas is 120 volumes, 150 volumes, and 350 volumes respectively. The volume of air required for the combustion of water gas restricts the volume of gas that can be used for the determination to about 25 c.c.; to secure greater accuracy, a mixture of oxygen and air can be used in the proportion of 35 c.c. of air and 25 c.c. of oxygen for 40 c.c. of water gas. It is preferable to combust this mixture in successive portions of about 30 c.c. at a time, rather than all together, especially if the worker is inexperienced with the apparatus; also, it is advisable to effect the combustion under slightly reduced pressure.

The oxygen can be generated in a small tube of the form shown in Fig. 95; about 2 g. of potassium chlorate are heated in the tube, which is attached by *a* to the rubber connection of the tap *d* (Fig. 93). After the contained air has been cleared out through *e*, which is placed under water, the taps *d* and *n* are opened to first clear out the capillary tube with oxygen, *n* then closed, and the oxygen introduced into A by lowering F.

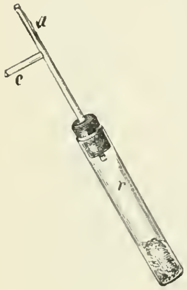

Fig. 95.

In order to obtain scientifically accurate results with this apparatus, the tubes M and D are graduated in mm., and readings taken of the barometer, the height of the columns of mercury in M and D, and the temperature of the water in the jacket round M, at each observation during the analysis. The volumes are then corrected to 0° and 1000 mm. pressure, by the formula:

$$V = \frac{v(B - b - e)}{1000\,[1 + (0{\cdot}00366t)]}$$

in which v is the volume of gas, B the height of the barometer (reduced to 0°), b the difference of level between M and D, and e the tension of aqueous vapour at the temperature of the experiment t. By adjusting the columns of mercury in M and D to the same level, after each determination, the correction for pressure is avoided; the correction for temperature is only required in cases where special accuracy is looked for, as the changes of temperature with a jacketed measuring tube are, as a rule, but slight during the interval of an analysis.

The calculation of the proportions of hydrogen, carbon monoxide, and methane follows from the volumetric changes according to the equations:

$$H_2 + O = H_2O \qquad CO + O = CO_2 \qquad CH_4 + 2O_2 = CO_2 + 2H_2O.$$

The contraction in the case of hydrogen (w) is $= \frac{3}{2}$, in the case of carbon monoxide (c) $= \frac{1}{2}$, and in that of methane (m) $= 2$: both carbon monoxide and methane form their own volume of carbon dioxide. Taking V as the total volume of combustible gases, n as the total contraction, and k as the total carbon dioxide formed, the resulting equations are:—

$$V = w + c + m. \qquad n = \tfrac{3}{2}w + \tfrac{1}{2}c + 2m. \qquad k = c + m.$$

Or,

$$\begin{aligned} \text{Hydrogen } (w) &= V - k. \\ \text{Carbon monoxide } (c) &= \tfrac{1}{3}k + V - \tfrac{2}{3}n. \\ \text{Methane } (m) &= \tfrac{2}{3}k - V + \tfrac{2}{3}n. \end{aligned}$$

Example of Analysis.

Volume of Gas taken, 60 *c.c.*

After absorption of Carbon dioxide, 56·1 ; *therefore* 3·9 *c.c. Carbon dioxide.*

After addition of Air, 116·1 ; *therefore* 60 *c.c. Air*, *containing* 47·4 *c.c. Nitrogen added.*

After combustion, 101·2 ; *therefore* $n = 14·9$.

After absorption of Carbon dioxide, 87·6 ; *therefore* $k = 13·6$.

After absorption of Oxygen, 85·7.

Of this Nitrogen, 47·4 *added as Air ; therefore* 38·3 *c.c. Nitrogen*, *and* $V = (56·1 - 38·3) = 17·8$.

Hence—

$$\begin{aligned} \textit{Volume of Hydrogen} &= 17·8 - 13·6 = 4·2 \text{ c.c.} \\ \textit{Volume of Carbon monoxide} &= 4·5 + 17·8 - 10 = 12·3 \text{ c.c.} \\ \textit{Volume of Methane} &= 9·1 - 17·8 + 10 = 1·3 \text{ c.c.} \end{aligned}$$

and the composition of the Gas—

Carbon dioxide . . .	3·9	or	6·5	per cent.
Hydrogen . . .	4·2	or	7·0	,,
Carbon monoxide . .	12·3	or	20·5	,,
Methane	1·3	or	2·2	,,
Nitrogen . . .	38·3	or	63·8	,,
	60·0	or	100·0	per cent.

A simple and very efficient form of gas-analysis apparatus, in which mercury is used as the confining liquid, has been recently described by W. A. Bone and R. V. Wheeler.[1]

W. H. Sodeau's Apparatus.[2]—This is based upon the gas-analysis apparatus of Macfarlane and Caldwell,[3] to which very many modifications and additions have been made, so that but little of the original arrangement remains. It can be used for the analysis of practically all ordinary gaseous mixtures, and is capable of giving results of great accuracy, with but moderate expenditure of time and trouble. Rapidity of working is obtained mainly by the adoption of (*a*), a ready, though highly accurate method of transference ; (*b*), pipettes in which the gas can be thoroughly agitated with the absorbent ; (*c*), a device showing at

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[1] *J. Soc. Chem. Ind.*, 1908, **27**, 10.

[2] *Ibid.*, 1903, **22**, 187. The editor is indebted to Dr W. H. Sodeau for this description of his apparatus ; it is made by Messrs Brady & Martin, Newcastle-on-Tyne.

[3] *J. West Scotland Iron and Steel Institute*, 1892, vol. i., No. 2.

a glance the correction for temperature and pressure. Contamination of the measuring tube is carefully guarded against.

The measuring tube M (Fig. 96) is graduated in $\frac{1}{10}$ c.c. divisions up to 50·5 c.c., so that no trouble arises if rather more than 50 c.c., the normal sample, should be drawn in. For special work, in which a considerable proportion of the gas remains unchanged, it is convenient to employ a measuring tube having a bulb and narrow graduated stem. A reliable verification of the graduations is essential. The top of the measuring tube is joined to a three-way, oblique bore, capillary stopcock N, arranged so that the capillary K may be placed in communication either with the interior of M, or with the detachable bent tube U containing water, and having a short length of rubber tubing connected to its outer end by means of a perforated rubber stopper (not shown in the figure). The zero point of the graduation is at the outer side of the plug of the stopcock N. The level tube L communicates with the measuring tube by means of a side branch, bent so as to exclude any air-bubbles entangled in the mercury. Its lower end is connected to a T-piece, one branch of which is provided with a stopcock and leads to the mercury reservoir, whilst the other is prolonged across the table to a point near the reading telescope, where it terminates in a piece of strong rubber tubing, the compression of which, by a broad screw clip, affords a means of accurately adjusting the level of the mercury, whilst looking through the reading telescope. In order to render the apparatus more compact, the reading telescope is placed on the opposite side of the gas-analysis table, instead of on a separate support; the graduations are consequently on the side opposite to that from which the stopcocks are manipulated.

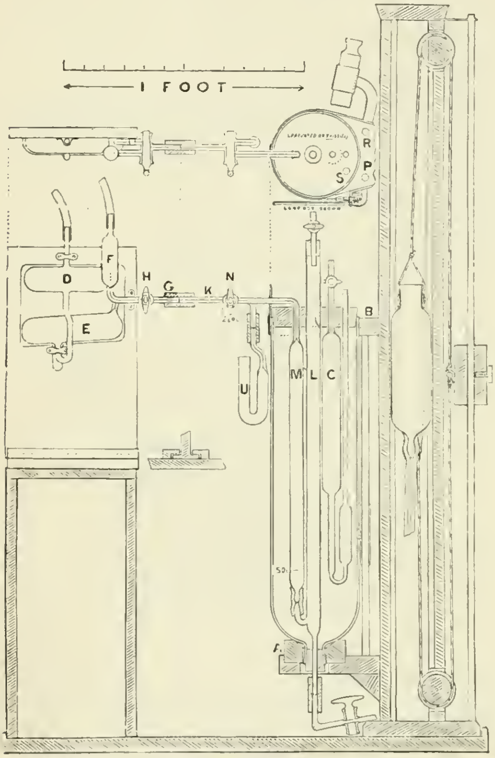

Fig. 96.

The illuminator is attached to a tubular fitting which slides on the rod P. It consists of a piece of ground glass having its upper half rendered opaque, and is adjusted so that only a narrow band of light is visible above the mercury. A 100-volt $2\frac{1}{2}$ candle-power lamp is attached.

The mercury reservoir can be adjusted without using both hands, and does not usually require clamping in position.

The "Kew principle" correction tube C is so called because, as in the "Kew" barometer, the disturbance of the level of the liquid is allowed for in the graduation, instead of being adjusted before each reading. It consists of a cylindrical bulb, closed above by a stopcock, and attached below to a U-tube graduated on the inner limb, and filled with water up to about the level of the zero mark; the outer end of the stopcock is attached to a bent glass tube, terminating in a short length of rubber tubing (not shown in the figure). At the beginning of an analysis the water is brought exactly to the zero mark by manipulating the rubber tube, and the stopcock is then closed. The volume of air contained in the instrument is such, that the water is displaced to the extent of one small division, by changes of temperature and atmospheric pressure which will cause a gas to alter its volume to the extent of 0·1 per cent.[1] These small divisions are viewed by means of a mounted lens sliding on the rod R, and are further subdivided by eye estimation. The corrections are thus read directly, in percentages, as easily as the temperatures would be read by means of a thermometer. The corrections may be kept very small, if the water in the jacket is syphoned off through the tube S before commencing an analysis, and brought to the probable average temperature of the room.

The absorption pipette is shown in Fig. 96. The absorption bulb E is inclined to the extent of about 1 in 20, in order to facilitate the return of the unabsorbed gas, and usually contains about 20 c.c. of the absorbent, confined over mercury. The bulb F contains clean mercury, and like the bulb E can be placed in communication with the capillary G by means of the three-way stopcock H. Rubber tubing is attached to the tubes, projecting upwards, from D and F, in order that the pressure in these bulbs may be varied by blowing or sucking, as required. Each pipette is mounted on a wooden support, which is slid into a very loosely fitting foot when in use, and afterwards replaced in a rack, inclined at an angle of not less that 35°, in order to relieve the pressure on the stopcock whilst out of use.

It is important that all capillary tubing employed in the apparatus should be of 1·0 to 1·5 mm. bore, and that the external diameter of the

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[1] A small division equals 0·05 c.c.; hence, external changes which would necessitate a 1 per cent. correction must cause 0·5 c.c. displacement of water. If this movement disturbs the level of the water to the extent of N mm., and if X c.c. = the volume of air in the instrument, it follows that

$$1{\cdot}01x = (x + 0{\cdot}5)\left(1 + \frac{N}{760 \times 13{\cdot}6}\right), \text{ and therefore } x = 50 + \frac{101\ N}{206{\cdot}7 - 2\ N}.$$

capillary G should be practically the same in all the pipettes. The external end of G must be quite flat, and at right angles to the axis of the tube.

The explosion pipette, Fig. 97, consists of a cylindrical bulb T, of about 220 c.c. capacity, connected to a mercury reservoir V. Wires are sealed in, near the top, for connection to a small induction coil, and a strip of paper, bearing rough graduations, is fixed to the back of the pipette. The arrangement lettered F, G, H, is common to all the pipettes.

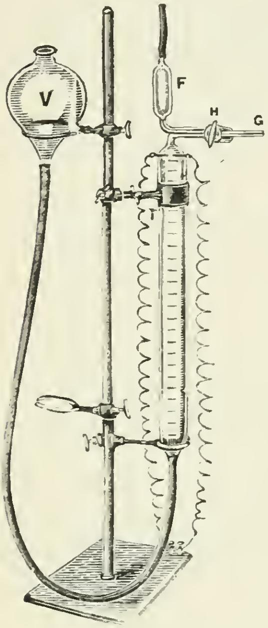

Fig. 97.

The combustion pipette, Fig. 98, is used when the proportion of combustible gases is not sufficient for a determination by explosion. Two nickel wires pass through the rubber stopper closing the bottom of the pipette, one being insulated from the mercury by means of a glass tube, and the two are connected above by means of a small spiral of platinum wire, W, about 0·25 mm. in diameter. This wire is heated by means of a 4-volt accumulator, the current being regulated by means of a short length of iron wire about 0·5 mm. in diameter.

The phosphorus pipette, Fig. 99, which it is sometimes convenient to use for the absorption of oxygen, has one bulb filled with thin sticks of phosphorus immersed in water, as in the Hempel apparatus (p. 209). It is clamped in a canister of water, which affords protection from light and also provides the means for readily raising the temperature of the phosphorus to about 20°. A small flap in the cover of the canister is removed whilst the gas is being returned to the measuring tube. No mercury is used in the bulb F.

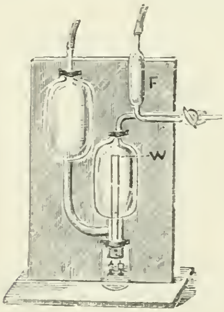

Fig. 98.

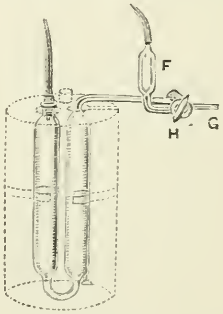

Fig. 99.

The following description of an analysis of a mixture of carbon dioxide, oxygen, carbon monoxide, hydrogen, methane, and nitrogen, will serve to illustrate the mode of working, when great accuracy is desired.

Introduction of the sample. The tube containing the gas is connected to a suitably bent capillary tube, preferably filled with mercury, which is in turn joined to the measuring tube capillary K (Fig. 96), by means of red rubber pressure tubing, after turning the stopcock N so that K is in communication with the tube U. The contents of the capillary are driven into U, and the cock N is then reversed, so that the required volume of gas can be drawn into the measuring tube M, by lowering the mercury reservoir. The cock N is then again reversed, the mercury roughly levelled, and a puff of air sent down the tube S, in order to stir up the water in the jacket.

Attachment of a pipette. The potash pipette is placed on the stand and the wetted end of the capillary G made to meet that of K, within the rubber tube. A little water is then sucked from U into the bulb F, and mercury allowed to run back and fill the capillary tubes.

Measurement of the sample. The stopcock leading to the mercury reservoir having been closed, and the level tube L being open to the atmosphere, the mercury is accurately levelled by means of the screw clip, and the volume of the gas read, by means of a reading telescope. The water in the correction tube is then adjusted to the zero mark.

Absorptions. To determine the carbon dioxide, the gas is driven over into the absorption pipette, followed by sufficient mercury to clear the capillaries, and the pipette is then rapidly rocked to and from the operator for two minutes, without disconnecting it from the measuring tube, so as to thoroughly churn up the absorbent; absorption is practically complete in twenty seconds, if the shaking is sufficiently vigorous. A little more mercury is then run over, so as to clear away the alkali from the bottom of the capillary attached to the absorption bulb, and the cock N reversed, so that the mercury in the capillaries runs into the tube U, instead of mixing with the clean mercury in the measuring tube. If any gas should be accidentally allowed to pass through the cock N into U, it is retained by the water, and can of course be drawn back without loss. The cock N is then again turned and the gas passed slowly into the measuring tube, the rate being controlled by the cock H, which is reversed as soon as the absorbent has filled the passage through its plug, so that the gas may be swept out of the capillaries by means of the clean mercury from the bulb F. The cock N is closed as soon as the mercury reaches it, and reversed after closing H, in order to facilitate the removal of the pipette. The next pipette (alkaline pyrogallol) is then connected up, the measurement of the residue carried out as described above, and a reading of the correction tube taken. It is convenient to enter the readings throughout the analysis in the following manner:—

Correction.	Reading.	Corrected Reading.	Difference.	Percentage.
·00	50·01 c.c.	50·01 c.c.	...	...
+ ·06 per cent.	33·24 c.c.	33·26 c.c.	16·75 c.c.	CO_2 33·50

The residual gas is then similarly shaken, for three minutes, with alkaline pyrogallol, at a temperature not below 16°. The decrease gives the amount of oxygen. To determine the amount of carbon monoxide, the residue is shaken for two minutes with cuprous chloride solution (taking care that the liquid is not allowed to absorb more than its own volume of carbon monoxide before being replaced), and then transferred directly to a second pipette, containing fresh cuprous chloride solution. After again shaking for two minutes, it is sent into a pipette containing about 2 c.c. of water, and then back into the measuring tube. It is a good practice to wash out the measuring tube during the absorption of carbon monoxide, in case any trace of potassium hydroxide has been introduced, as it would prematurely absorb part of the carbon dioxide subsequently formed by explosion. Air is drawn in after the water used in the washing has been expelled, and the mercury then allowed to re-enter very slowly, in order that the film of water may be properly squeezed off the sides of the tube. After the carbon monoxide has been determined, oxygen, stored over mercury in one of the ordinary absorption pipettes, is added in excess, and the mixture measured. If the oxygen is prepared by electrolysis it should be freed from traces of hydrogen, *e.g.* by treatment in a combustion pipette kept for that purpose.

Hydrogen and methane are estimated by means of the combustion pipette (Fig. 98), if only small amounts are present, but the explosion pipette (Fig. 97) is employed when the proportions are sufficient. The mode of transference to these pipettes is the same as with the absorption pipettes, but in returning the gas to the measuring tube, mercury from the bulb V (instead of from the bulb F) may be used for driving the gas out of the capillary. When the combustion pipette is employed, the current is switched on as soon as the top of the glass insulating tube has become exposed, and the coil is maintained at a very bright red heat for two or three minutes, in order that complete combustion may be effected.

Before passing a spark through a mixture in the explosion pipette, the gas must be expanded (by lowering the mercury reservoir), to such an extent that no appreciable amount of nitrogen will be oxidised ; if, however, the expansion is carried too far, the combustible gases will not be burnt completely. This point merits more attention than it appears to have generally received. If the expanded volume is markedly less than ten times the volume of hydrogen, measured under atmospheric pressure, plus twenty times that of the methane, the amount of nitrogen oxidised is usually sufficient to cause the condensed moisture to have a pronounced action upon the mercury; in the absence of very definite information, it seems best to expand to an ample extent and to subsequently employ the combustion pipette to ascertain whether any traces of unburnt combustible gas remain.

After combustion or explosion, the residue is measured and the resulting carbon dioxide absorbed. From the volume of carbon dioxide produced and the total contraction, the proportions of the methane and hydrogen are calculated. The nitrogen is determined by difference. Finally, the excess of oxygen is determined by means of pyrogallol or phosphorus, as a check upon the other measurements.

Absorbents which attack mercury, such as fuming sulphuric acid, can usually be employed in the ordinary absorption pipettes, an appropriately filled guard tube being attached to the bulb D. Of course, no mercury is used to confine these liquids, and the mercury in the capillaries is very carefully driven into the bulb F before transferring the gas. After absorption, the gas may be transferred directly to the potash pipette, and thence to the measuring tube.

Other accessories. Almost any form of absorption or combustion device can be employed in conjunction with this apparatus, if it is fitted with a horizontal capillary stopcock, or preferably with the usual arrangement of the bulb and three-way stopcocks, F, G, and H.

ABSORPTION COEFFICIENTS OF THE COMMONER GASES IN WATER

In the following table the absorption coefficients of the commoner gases in water at 15°, are given, as determined by Bunsen (propylene by v. Than). These values must be taken into consideration in all cases in which gases are collected or analysed over water.

Propylene	0·237	Carbon monoxide	0·024
Ethylene	0·162	Hydrogen	0·019
Methane	0·039	Oxygen	0·030
Carbon dioxide	1·002	Nitrogen	0·015

More recent determinations by L. W. Winkler give the following values for oxygen,[1] nitrogen,[2] hydrogen,[3] and carbon monoxide;[4] the

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[1] *Ber.*, 1891, **24**, 3609.

[2] *Ibid.*, 1891, **24**, 3606.

[3] *Ibid.*, 1891, **24**, 99.

[4] *Z. physikal. Chem.*, 1892, **9**, 173.

coefficients are stated for every degree between 0° and 100°, in the case of oxygen and of nitrogen, in the original papers.

Coefficient of Solubility at	10°	12°	14°	16°	18°	20°
Oxygen	0·038	0·036	0·035	0·033	0·032	0·031
Nitrogen	0·018	0·018	0·017	0·016	0·016	0·015
Hydrogen	0·020	0·019	0·019	0·019	0·018	0·018
Carbon monoxide	0·028	...	...	...	...	0·023

THE CALORIFIC VALUE OF GASEOUS FUEL

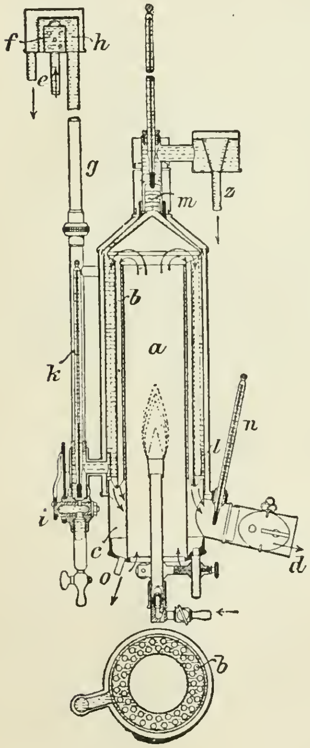

FIG. 100.

The calorific power of heating and of illuminating gas can be calculated from that of its constituents, as determined by analysis, but the method involves a complete gas analysis, and is unsatisfactory on account of the difficulty of obtaining an accurate determination of the individual hydrocarbons (*cf.* Vol. II., Gas Manufacture). A direct determination of the calorific value is accordingly advantageous. The calorimeters devised by Junkers[1] and by Boys are generally used for this determination; that of F. Fischer[2] will also be described in this section.

Junkers' Gas Calorimeter.—In this apparatus, the heat generated by the flame of burning gas is transmitted to a current of water flowing at a constant rate, and measurements are made of the volume of gas burnt, the quantity of water heated, the difference in temperature of the water on entering and leaving the apparatus, and the quantity of water condensed from the products of the combustion. The gas is burnt in a large Bunsen burner (Fig. 100), in the combustion chamber *a*, which consists of an annular copper vessel, the annular space being traversed by a number of copper tubes *b*, connecting the top with the bottom of the chamber. The products of combustion pass through these tubes in a downward direction, the condensed water being collected at *o*, and the

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[1] *Cf.* H. Kühne, *J. Soc. Chem. Ind.*, 1895, 14, 631.

[2] *Taschenbuch für Feuerungstechniker*, 5th edition, 1883, p. 5.

waste gases escaping through the side tube *d*. The current of water enters at *e*, where it passes through a sieve *h*, and enters the calorimeter through *g* and *i*, thus circulating in an opposite direction to that of the products of combustion, whereby complete cooling of the latter, to the temperature of the water, is effected. The water, after passing through the annular chamber, goes over a series of baffle plates at *m*, to ensure thorough mixing, and then passes out through the overflow *z*, where it is collected and measured. The pressure of water is kept constant by the two overflows at *h* and *z*, the water being run into *h* at a greater rate than it passes through the calorimeter; the rate of flow is regulated by the cock *i*. The temperature of the entering water is taken by the thermometer *k*, that of the exit water by the thermometer above *m*. The whole instrument is enclosed in a cylindrical air-jacket of polished or plated copper, to prevent radiation.

The whole apparatus, as arranged for actual experiment, is shown in Fig. 101. The gas to be tested is measured by a small wet meter, provided with a thermometer, and is passed through a governor, to ensure a steady pressure of gas at the burner; a water-pressure gauge is attached to the governor, which indicates the pressure, above that of the atmosphere, at which the gas is measured. As the water supply may vary considerably in temperature, even within a short period of time, if taken directly from a tap, it is preferable to have a large reservoir for its storage. Pfeiffer[1] recommends a sheet-zinc tank of 60 litres capacity (H, Fig. 101), provided with a pipe *w*, which serves both for filling and discharging, a glass gauge, and an overflow pipe *u*; the pipe *w* is connected with the pressure box of the calorimeter, through the tap *v*. The experiment should be so regulated that the temperature of the exit gases at *s* (Fig. 101) is the same as that of the laboratory, so that they are only saturated with the quantity of moisture corresponding to this temperature. Instead of measuring the water collected from *c*, it may be weighed in the bottle F, of about 10 litres capacity, the weight of the empty bottle having been previously determined.

The condensed water from the calorimeter is collected in the measuring cylinder *d* (Fig. 101), which is placed in position after the gas-meter index has completed a revolution, from the start of the experiment, and the collecting continued for a corresponding period, after the bottle F has been removed.

To carry out a test, the water is first turned on, and when it is running from both overflows, the gas is lighted and the speed of the water regulated by the cock *i*, so that there is a difference of from 10°

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[1] *Note.*—These recommendations, in respect to the use of the Junkers' calorimeter and the accompanying figure, are incorporated from Dr Pfeiffer's contribution on Gas Manufacture in Vol. II. of the German edition.—C. A. K.

to 20° between the inlet and outlet thermometers; illuminating gas is burnt at the rate of from 100 to 300 litres (4 to 11 cubic feet) per hour, producer gas at the rate of from 400 to 1000 litres (14 to 35 cubic feet). When the difference in temperature of the two thermometers is nearly constant and the condensed water is dripping regularly into *d*, the test can be begun. This is done by waiting until the gas-meter index passes any desired point, and then quickly introducing the outlet water-tube *c*, into a suitable measuring vessel; a series of readings of the thermometers are taken whilst about 28 litres (one cubic foot) of gas is burnt, and the volume of gas and of collected water measured. The inlet thermometer *k* should be read every minute, and the outlet thermometer (T, Fig. 101) every half minute.

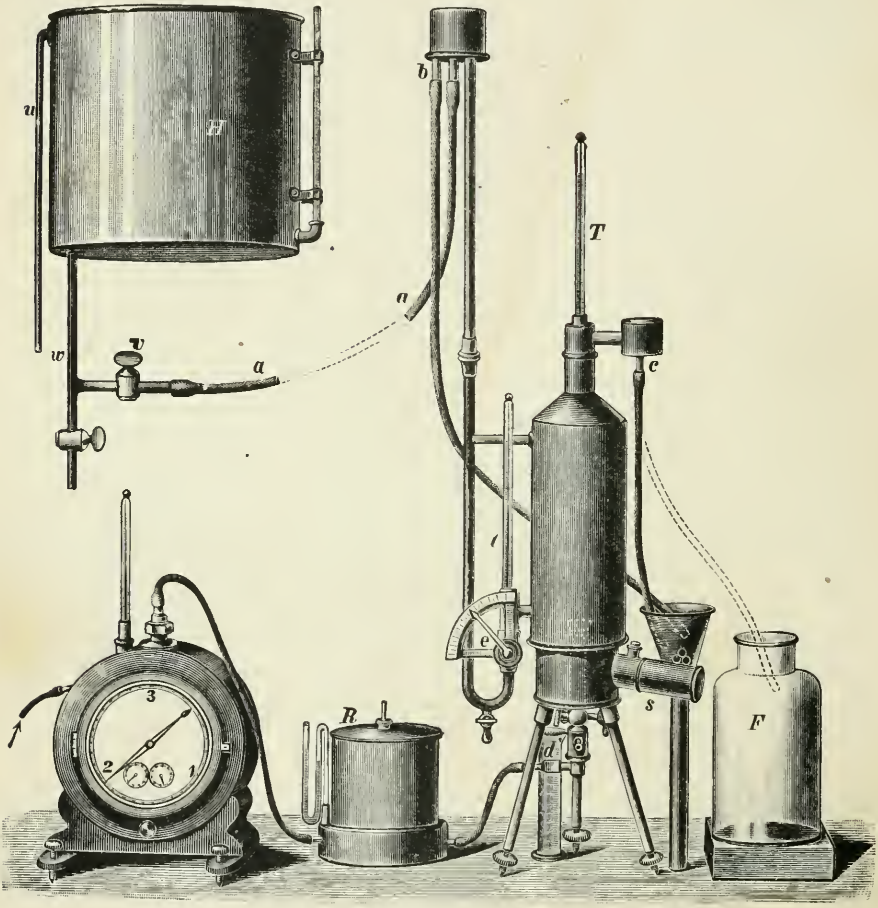

Fig. 101.

The calorific value is,

$$= \frac{\text{Weight of water} \times \text{temperature difference}}{\text{Volume of gas consumed}},$$

the volume of gas being corrected for temperature and pressure.

The value thus obtained represents the calorific power of the gas, when the water formed by the combustion is converted into the liquid state in the calorimeter. To obtain the calorific value when the water formed escapes as steam, the latent heat of the condensed water must be deducted; the quantity of heat evolved by each c.c. of condensed water may be taken, with sufficient accuracy for most purposes, as 0·6 big calories (the amount of heat required to raise 1000 g. of water 1° C.), and this value, multiplied by the number of c.c. of water condensed and divided by the gas consumed, will give the total heat to be deducted from the gross or "higher" calorific value, in order to give the net or "lower" calorific value of the gas, with the water formed in the combustion remaining as steam. The result in calories, multiplied by 3·97, gives the calorific value in British thermal units.

No further corrections are necessary, and the results are in every respect satisfactory if the experimental conditions are properly carried out. It is important that the determinations should be made in a room free from any considerable variations of temperature.

If a large flame is used, the combustion is apt to be incomplete; it is accordingly recommended to ascertain, by a preliminary experiment, that the waste gases contain several per cent. of oxygen, as otherwise the determination of the calorific value may be 5 per cent. or more too low (F. Fischer).

Example of Determination.

Volume of gas consumed (5 revolutions of meter index, at 3·06 litres per revolution)	15·3 litres.
Weight of water	5310 g.
Temperature of inlet water, constant	13°·8
Temperature of outlet water: 28·1 – 28·15 – 28·15 – 28·1 28·1 – 28·1 – 28·1 – 28·1 – 28·1 – 28·1	Mean: 28°·11
Temperature difference	14°·31
Volume of condensed water	14 c.c.
Temperature of room	22°
Barometer	766 mm.

Gross calorific value per cubic metre, at 15° C. and 760 mm.

$$= \left(\frac{5\cdot310 \times 14\cdot31}{0\cdot0153}\right) \times \frac{273+22}{288} \times \frac{760}{766}$$

$$= 5082.$$

Net calorific value per cubic metre, at 15° C. and 760 mm.

$$= \frac{(5\cdot310 \times 14\cdot31) - 0\cdot6 \times 14}{0\cdot0153} \times \frac{273+22}{288} \times \frac{760}{766}$$

$$= 4533.$$

Owing to the small quantity of condensed water collected in a single experiment, Pfeiffer[1] regards the above method of arriving at the net calorific value as somewhat inaccurate, and as the result of his own observations, is of the opinion that it can be best calculated from the gross calorific value on the basis of independent experiments in which 50 to 70 c.c. of condensed water are collected. From numerous determinations, he finds that the net value is 11·1 per cent. less than the gross value, in the case of gas made from English or from Westphalian coal and, as an average, 8·6 per cent. less in the case of carburetted water gas. From these data, the net calorific value may be calculated directly from the experimental determination, without reference to the volume of condensed water formed.

To facilitate the correction of the calorific value for the volume occupied by the gas at 15° and 760 mm., Pfeiffer has constructed the subjoined table (p. 231), in which the figures are given, which must be added to or subtracted from the value :—

$$\frac{\text{Weight of water} \times \text{temperature difference}}{\text{Volume of gas consumed}}.$$

The table is calculated for gases having a calorific value of 5000 calories per cubic metre; the corrections given in the table are sufficiently near to those required for gases, with a calorific value within ± 200 calories of this limit, to be applicable also within this wider range. The correction, for instance, at 22° and 750 mm. for gases of 4800 and 5200 calories per cubic metre respectively, is 0·18 and 0·196, against 0·189 in the table.

Calculations in cubic feet and corrected to 60° F. and 30-inch pressure are similarly made, the tables used in the determination of the illuminating power of coal gas being employed for the latter corrections.

Boys' Gas Calorimeter.[2] — This apparatus is prescribed by the *Metropolitan Gas Referees* (1906), for testing the calorific value of illuminating gas. It has been designed with the object of providing ample space for the circulation of the stream of gases, so that they pass slowly and freely through the instrument, and are thus effectively exposed to the cooling surfaces. The water content of the instrument is reduced to the smallest quantity, so that the outflowing water attains its ultimate temperature very quickly after the gas is lighted. The whole of the circulating water takes the same course continuously, being debarred from any parallel or alternative routes, and thus unequal heating and the attendant irregularity of the temperature at the outflow are avoided. The small content of water suffices to abstract the whole of the heat from the slowly travelling stream of gases, owing partly to

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[1] *Loc. cit.;* and *J. Gasbeleucht*, 1904, **44**, 684.

[2] *Proc. Roy. Soc.*, 1906, **77**, Series A. 122. The apparatus is made by J. J. Griffin & Sons, Kingsway, London.

Table for Correcting the Volume of Gases having a Calorific Value of 5000 Calories (±200 Calories), per cubic metre, to 15° C. and 760 mm.

The figures give the amount to be added to the ascertained calorific value ; the inclined figures are minus values.

Mm.	10°	11°	12°	13°	14	15°	16°	17°	18°	19°	20°	21°	22°	23°	24	25°	26°	27°	28°	29°	30°
745	12	29	47	65	83	100	118	136	153	171	189	206	224	242	260	277	295	313	331	348	365
746	6	23	41	59	77	94	112	130	147	165	183	200	218	236	254	271	289	307	325	342	359
747	*1*	17	34	53	70	88	105	123	140	158	176	193	210	229	247	264	281	299	318	334	352
748	*8*	9	27	46	63	81	98	116	134	151	169	186	204	222	240	257	274	291	310	327	344
749	*15*	2	20	39	56	74	91	109	127	144	162	178	196	214	232	249	267	284	303	320	337
750	*22*	*4*	13	31	49	66	84	101	119	137	154	171	189	207	225	242	261	277	295	313	330
751	*27*	*10*	7	25	43	60	77	95	113	131	148	165	183	201	219	236	255	272	289	307	323
752	*34*	*17*	0	19	36	45	71	89	106	124	141	158	176	194	212	229	248	264	282	299	316
753	*40*	*24*	*6*	12	29	47	64	82	99	117	135	151	169	187	205	222	241	257	274	291	309
754	*48*	*31*	*14*	5	23	40	58	75	93	110	128	144	162	180	198	215	234	249	267	284	302
755	*54*	*36*	*20*	*1*	17	34	52	69	87	104	122	138	156	174	192	208	228	243	261	278	295
756	*60*	*43*	*26*	*8*	9	27	44	62	79	97	114	131	148	166	184	201	220	236	254	271	288
757	*68*	*50*	*33*	*15*	2	20	37	55	72	90	107	124	141	159	177	194	213	229	247	264	281
758	*74*	*57*	*39*	*22*	*4*	13	30	48	65	83	100	117	135	152	170	187	206	222	240	257	273
759	*80*	*62*	*45*	*27*	*10*	7	24	42	59	77	94	111	129	146	164	181	200	216	234	250	267
760	*86*	*70*	*52*	*34*	*17*	**0**	18	35	53	70	88	106	122	140	157	174	193	208	226	243	260
761	*93*	*77*	*59*	*40*	*24*	*6*	10	28	46	63	81	97	114	133	150	166	186	201	219	236	253
762	*100*	*83*	*66*	*48*	*31*	*14*	3	21	39	56	74	90	107	125	142	159	178	194	212	229	246
763	*105*	*89*	*72*	*55*	*37*	*21*	*2*	16	32	50	67	84	101	119	137	153	172	188	206	222	240
764	*112*	*95*	*79*	*61*	*44*	*27*	*9*	8	25	43	60	77	94	112	130	146	165	181	199	216	232
765	*119*	*102*	*85*	*68*	*51*	*34*	*16*	1	19	36	54	70	88	105	123	140	158	174	192	208	225
766	*125*	*107*	*91*	*74*	*57*	*39*	*22*	*5*	13	30	48	64	82	99	117	134	152	168	186	202	219
767	*132*	*115*	*97*	*81*	*63*	*47*	*28*	*12*	6	23	41	58	75	93	110	126	145	160	178	195	212
768	*138*	*122*	*104*	*88*	*71*	*54*	*36*	*20*	*1*	17	36	51	67	86	102	119	139	153	171	188	205
769	*144*	*127*	*110*	*93*	*77*	*59*	*42*	*25*	*6*	10	30	44	62	79	97	113	131	147	165	182	199
770	*150*	*134*	*116*	*100*	*83*	*66*	*49*	*32*	*14*	3	23	37	55	73	90	106	125	140	158	175	192
771	*157*	*140*	*124*	*106*	*90*	*73*	*56*	*38*	*21*	*3*	17	30	48	65	83	99	118	134	151	168	184
772	*163*	*146*	*129*	*112*	*95*	*79*	*61*	*44*	*26*	*9*	8	24	42	59	77	93	112	128	145	162	178
773	*169*	*152*	*136*	*119*	*102*	*85*	*68*	*51*	*33*	*16*	1	18	35	53	70	87	105	122	139	154	171
774	*175*	*158*	*141*	*125*	*107*	*91*	*74*	*57*	*38*	*22*	*4*	12	29	47	64	81	99	116	132	148	165
775	*182*	*165*	*148*	*130*	*113*	*96*	*80*	*62*	*45*	*28*	*11*	5	23	40	58	74	93	109	125	141	158

the avoidance of parallel routes, but mainly by reason of its flow through a pipe of small diameter, the heat-collecting power of which is greatly increased by attached wires.

The calorimeter is shown in vertical section in Fig. 102. It consists of three parts, which may be separated, or which, if in position, may be turned relatively to one another about their common axis. The parts are (1), the base R, carrying a pair of burners B, and a regulating tap. The upper surface of the base is covered with a bright metal plate, held in place by three centring and lifting blocks C. The blocks are so placed as to carry (2), the vessel D, which is provided with a central copper chimney E, and a condensed water outlet F. Resting upon the rim of the vessel D are (3), the essential parts of the calorimeter, attached to the lid G. At the centre, where the outflow is situated, there is a brass box, which acts as a temperature-equalising chamber for the outlet water. Two dished plates of thin brass, K, are held in place by three scrolls of thin brass, LLL. The lower or pendent portion of the box is kept cool by water, circulating through a tube which is sweated on to the outside of the bell. Connected to the water channel at the lowest point, by a union, are six turns of copper pipe, such as is used in a motor car radiator, of the kind known as Clarkson's. In this, a helix of copper wire threaded with copper wire is wound round the tube, and the whole is sweated together by immersion in a bath of melted solder. A second coil of pipe, of similar construction, surrounding the first, is fastened to it at the lower end by a union. This terminates at the upper end in a block, to which the inlet water box and thermometer holder are secured by a union, as shown at O An outlet water box (P) and thermometer holder are similarly secured above the equalising chamber. The lowest turns of the two coils N are immersed in the water, which in the first instance is put into the vessel D.

Between the outer and inner coils N is placed a brattice (Q), made of thin sheet brass, containing cork dust, to act as a heat insulator. The upper annular space in the brattice is closed by a wooden ring, and this end is immersed in melted rosin and beeswax cement, to protect it from any moisture which might condense upon it. The brattice is carried by an internal flange, which rests upon the lower edge of the casting H. A cylindrical wall of thin sheet brass, a very little smaller than the vessel D, is secured to the lid, so that when the instrument is lifted out of the vessel and placed upon the table, the coils are protected from injury. The narrow air space between this and the vessel D also serves to prevent interchange of heat between the calorimeter and the air of the room.

The two thermometers for reading the water temperatures, and a third for reading the temperature of the outlet air, are all near together and at the same level. The lid may be turned round into any position,

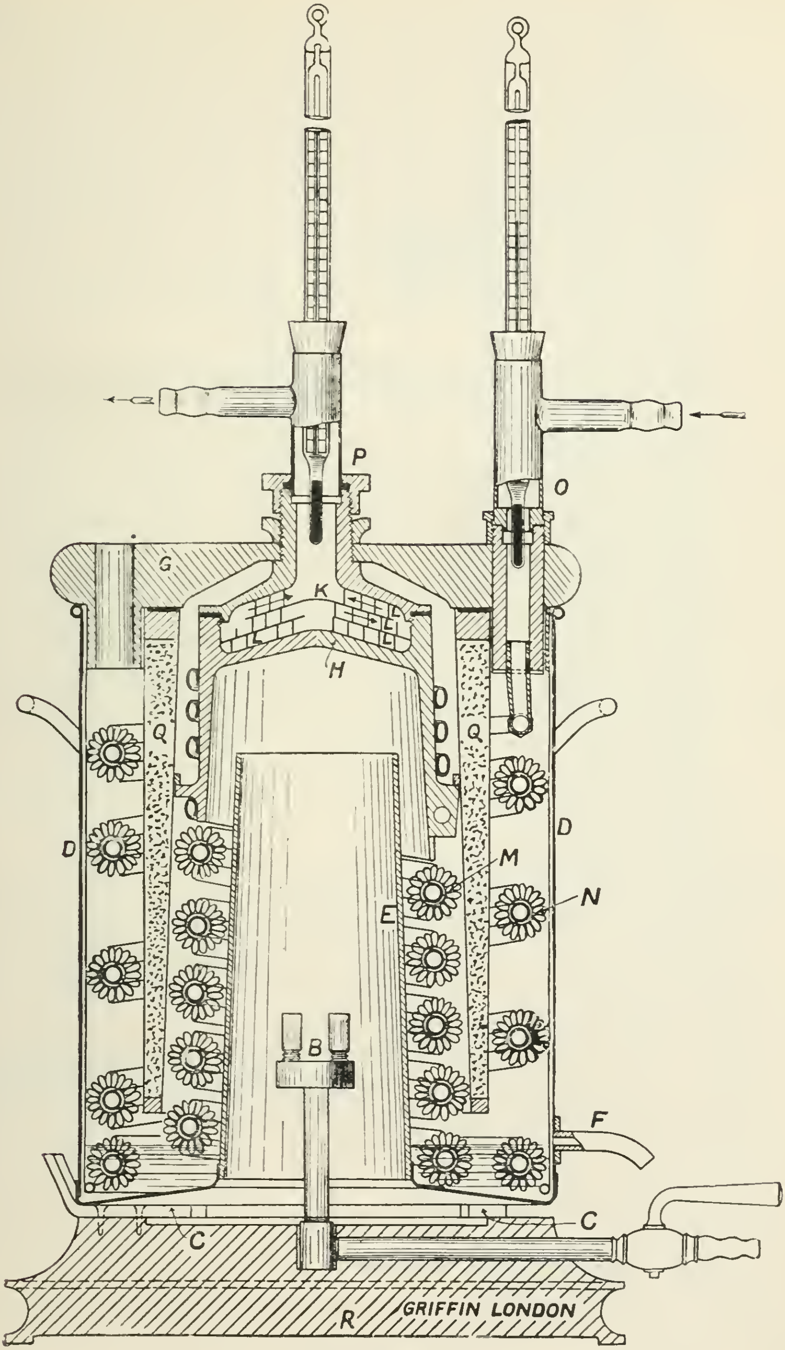

Fig. 102 (⅓ Nat. Size).

relatively to the gas inlet and condensed water drip, that may be convenient for observation, and the inlet and outlet water boxes may themselves be turned, so that their branch tubes point in any direction.

The general arrangement of the apparatus, as set up for a test, is shown in Fig. 103, the gas being first passed through a meter and balance governor, before being led to the calorimeter. The gas supply is connected up to the central tube at the back of the meter and thence to the governor, preferably by means of composition piping. The pipe leading from the governor should terminate in a tap with a nozzle, to which a short length of rubber tubing is attached for connecting to the calorimeter.

A regular supply of water is maintained, by connecting one of the two outer pipes of the overflow funnel, shown in Fig. 103, to a small tap over a sink. The overflow funnel is fastened to the wall about one metre above the sink, and the other outer pipe is connected to a tube, in which there is a diaphragm with a hole 2·3 mm. in diameter. This tube is connected to the inlet pipe of the calorimeter. A piece of stiff rubber tubing, long enough to carry the overflow water clear of the calorimeter, is slipped on to the outflow branch, and the water is turned on so that a little escapes by the middle pipe of the overflow funnel, and is led by a third piece of tube into the sink. The amount of water that passes through the calorimeter in four minutes should be sufficient to fill the graduated vessel shown in Fig. 103 to some point above the lowest division, but insufficient to come above the highest division in five minutes. If this is not found to be the case, a moderate lowering of the overflow funnel or reaming out of the hole in the diaphragm will effect the necessary correction.

The thermometers for reading the temperature of the inlet and outlet water are divided into tenths of a degree, and are provided with reading lenses and pointers that slide upon them. The thermometers are held in place by corks, fitting the inlet and outlet water boxes. The thermometers for reading the temperature of the air near the instrument and of the outlet gases are divided into degrees.

The flow of air to the burners is determined by the degree to which the passage is restricted, at the inlet and at the outlet. The blocks C (Fig. 102), which determine the restriction at the inlet, are made of metal, about 5 mm. thick, while the holes round the lid which determine the restriction at the outlet, are five in number and are 16 mm. in diameter. The thermometer used for finding the temperature of the effluent gas is held by a cork in the sixth hole in the lid, so that the bulb is just above the upper coil of pipe.

The calorimeter should stand on a table by the side of a sink, so that the condensed water and hot-water outlets overhang and deliver into the sink, as shown in Fig. 103. A glass vessel is provided of the size

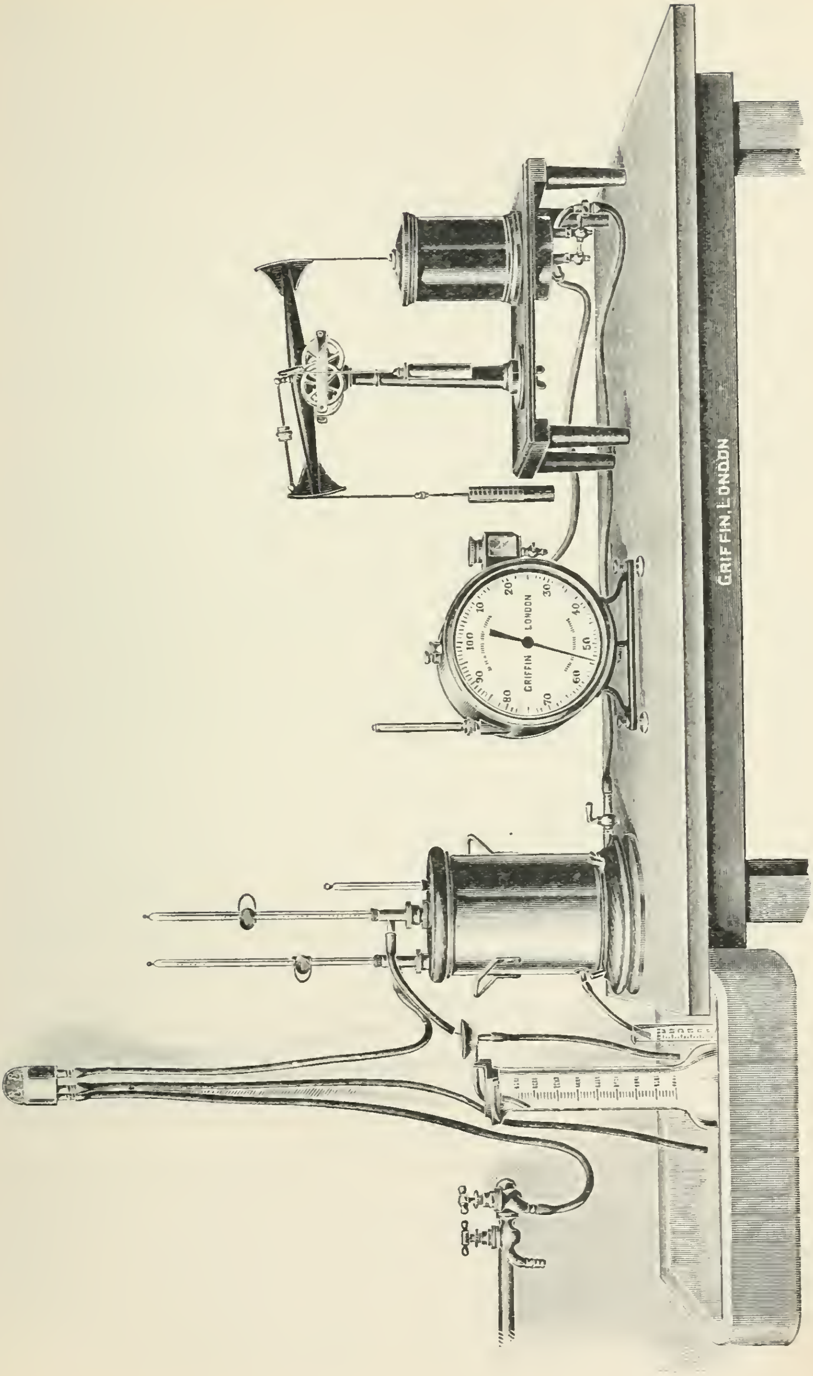

Fig. 103.

of the vessel D, which should be filled with water, in which sufficient carbonate of soda is dissolved to make it definitely alkaline. The calorimeter, when not in use, is lifted out of its vessel D and placed in the alkaline solution, and left there until it is again required. The liquid should not come within two inches of the top of the vessel, when the calorimeter is placed in it. The liquid must be replenished from time to time and its alkalinity maintained.

The measuring vessel, shown in Fig. 103, carries a change-over funnel, which is placed beneath the short tube attached to the hot-water outlet. One side of the funnel delivers into the sink, and the other delivers into a tube, which directs the water into the vessel.

Full details for carrying out a test are given in the *Notification of the Metropolitan Gas Referees for* 1906;[1] the above description of the apparatus is taken from this notification.

Fischer's Gas Calorimeter.[2]—This form of calorimeter (Fig. 104), consists of a wooden vessel B, in which nickel-plated copper vessels A and C are contained. A is suspended from the top of B as shown, and C is fitted into B by the water-tight junction at *v*, which should be greased before use. The detachable cover D is provided with an attachment at *t* for inserting a thermometer, and to carry the stirrer R; the inner vessel C is expanded into three lenticular chambers, each of which contains a sheet of metal *n*, serrated round the edge, the object of which is to promote intimate contact between the products of combustion and the inner surface of the calorimeter. The whole vessel is supported on the feet F. The burner E is supported by the socket *f* and the arm *m*, and is so arranged that it can be readily adjusted into position, by means of the tongue *a* and a pin below *f*. A small inverted cone of nickel gauze is placed in the tube of the burner, to prevent the gas striking back; a cone, preferably of platinum gauze, with its apex upwards, may also be fitted to the top of the burner tube. Air enters at the inclined plate *s*, the direction of which serves to retain the condensed water in the calorimeter, and the waste gases leave through *b*.

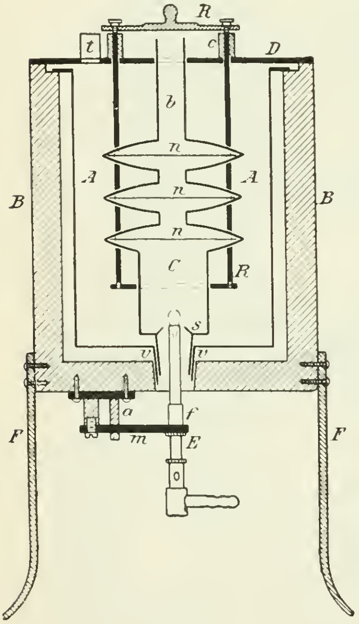

Fig. 104.

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[1] Published by Wyman & Sons, Fetter Lane, London, E.C. Price 1s. 6d.

[2] *Fischer's Jahresber.*, 1901, 47, 50.

To carry out a determination, the required quantity of water is placed in A, the inner vessel C is placed in position, the cover D put on, and a thermometer inserted at *t*. The water is agitated by the stirrer until the temperature is constant, and the burner drawn down below the body of the calorimeter and attached to the gas supply; the gas should be passed through the meter for some time previous to the determination, in order to saturate the contained water. The burner is then lighted, and quickly introduced into the position shown; the flame is adjusted for complete combustion, this adjustment being best determined by a preliminary experiment so as to ensure an excess of 5 per cent. of oxygen in the waste gases. In testing semi-water gas or producer gas, the air-holes at the bottom of the burner are closed; in the case of difficultly combustible gases, such as blast-furnace gas, it is recommended to supply oxygen (about one-fifth of the volume of the gas) through a tube fixed in the centre of the burner. The volume of gas required for a determination is 1 litre of coal gas, $1\frac{1}{2}$ to 2 litres of water gas, and 3 litres of producer or of semi-water gas. When the desired volume of gas has been burnt, the rubber tube connected with E is closed by pressing, and the temperature of the water in the calorimeter read, after agitating with the stirrer for two minutes.

The increase of temperature, multiplied by the heat equivalent of the calorimeter, gives the calorific value of the total gas burnt, which can be calculated to the gross value per cubic metre at normal pressure, and 15° C, as described above. To obtain the net calorific value of the gas, the water in C, in which vessel the greater part of the water formed in the combustion is condensed, is weighed; this is effected by first emptying the water out of A, and then detaching and weighing C, after carefully drying it outside, the weight of the empty vessel having been previously ascertained. A determination can be made in a few minutes, and the volume of gas used is much less than that required for the Junkers calorimeter; the apparatus may accordingly be advantageously used as a check on working conditions, and also when the gas sample cannot be tested *in situ*.

An apparatus for the determination of the calorific value of small quantities of gas (2 to 3 litres) has been described by Hempel.[1]

THE LOSS OF HEAT FROM CHIMNEY GASES

The loss of calorific effect in the combustion of fuel, owing to the retention of heat by the chimney exit gases, can be calculated from the following considerations. If the average percentage composition of the chimney gas is *k* parts carbon dioxide, *o* parts oxygen, and *n* parts nitrogen, and that of the air for the com-

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[1] *J. Soc. Chem. Ind.*, 1901, **20**, 880; *Z. angew. Chem.*, 1901, **14**, 713.

bustion, x parts oxygen and z parts nitrogen, then the ratio v of the quantity of air used, to that theoretically required is expressed by the equation :—

$$v = \frac{x}{x-(zo : n)} \text{ or } \frac{n}{n-(zo : x)} \text{ or } \frac{21}{21-(790 : n)}$$

with air containing 21 per cent. of oxygen. Since 1 kilo carbon gives 1·854 cb.m. of carbon dioxide on combustion, 1 kilo of fuel, containing c per cent. of carbon (after deducting any unburnt carbon left in the ash or slag), gives $1{\cdot}854 \times \frac{c}{100} = K$ cb.m. of carbon dioxide (at 0° and 760 mm.); the resulting chimney gases will include, in addition, $K \times \frac{o}{k} = O$. cb.m. of oxygen, and $K \times \frac{n}{k} = N$. cb.m. of nitrogen. The total weight of water-vapour W, contained in the chimney gases, consists of that derived from the moisture present in the fuel, as ascertained by analysis, that formed by the combustion of the hydrogen, and that contained in the air used in the combustion. With s as the percentage of sulphur in the fuel, the total volume of the products of combustion is :—

$$K + \frac{K(o+n)}{k} + \frac{2s}{286{\cdot}4} + \frac{W}{0{\cdot}805} \text{ cb.m., at } 0^\circ \text{ and } 760 \text{ mm.}$$

(286·4 = weight of 1 cb.m. of sulphur dioxide ; 0·805 = weight of 1 cb.m. of water-vapour).

The loss of heat is calculated by multiplying the volume of each gas by its specific heat, and by the difference between the temperature of the air supply and that of the exit gases ; the total of these factors gives the heat loss in calories. The loss due to incomplete combustion can be calculated from the calorific value of the unburnt coal in the furnace residue and of the combustible constituents of the chimney gases, carbon monoxide, methane, hydrogen, and soot.[1]

For practical purposes, a shortened formula proposed by Lunge,[2] dependent upon the determination of carbon dioxide only, is to be recommended. The proportion of oxygen and nitrogen in the waste gases is taken by difference. If n = the volume per cent. of carbon dioxide, then $100 - n$ = the volume per cent. of oxygen plus nitrogen ; and since 1 kilo of carbon forms 1·854 cb.m. of carbon dioxide on combustion, the volume of oxygen plus nitrogen in cb.m. per kilo of carbon is :—

$$= 1{\cdot}854 \times \frac{100-n}{n}.$$

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[1] For further details, *cf.* Fischer, *Taschenbuch für Feuerungstechniker*, 5th edition, 1885.

[2] *J. Soc. Chem. Ind.*, 1889, **8**, 531 ; and *Z. angew. Chem.*, 1889, **2**, 240.

If t' = temperature of the chimney gases, t = temperature of the air, c = specific heat of 1 cb.m. carbon dioxide (0·41 up to 150° and 0·43 to 0·46 between 150° and 350°), and c' = specific heat of 1 cb.m. of nitrogen (about 0·31), then the loss of heat (L) per kilo of carbon burnt, expressed in calories, is :—

$$L = 1{\cdot}854(t' - t)c + 1{\cdot}854(t' - t) \times \frac{100 - n}{n} c'.$$

Since the calorific value of 1 kilo of carbon is 8·08 calories, then

$$\frac{100 \times L}{8{\cdot}08} = \text{Percentage loss of heat by the waste gases.}$$

DETERMINATION OF THE TOTAL SULPHUR IN HEATING GASES

This determination, which is occasionally desirable, can be carried out by means of the apparatus shown in Fig. 105 ($\frac{1}{10}$ actual size). The gas supply, after passing the experimental meter, is burnt in the small Bunsen burner B, at the bottom of the adapter C; the latter is fitted into the bulb tube *n*, at *v*, either by a cork or by an asbestos ring. The tube is surrounded by a condenser K, the water supply of which enters at *a* and leaves at *n*. The water formed in the combustion condenses in the tube *nn*, and there absorbs the sulphurous and sulphuric acids, the liquid products being finally collected in F. The sulphur content is determined by titration with *N*/10 alkali, after first oxidising the sulphurous acid with hydrogen peroxide; or a test-tube, containing ammonium hydroxide, may be placed by the side of the burner, during the combustion, in order to ensure a more complete condensation of the sulphur dioxide, and the sulphuric acid determined gravimetrically. The current of gas is regulated so that there is an excess of 4-6 per cent. of free oxygen, as can be determined by taking a sample of the exit gases at O; with good condensation, about 50 c.c. of liquid are collected per 50 litres of gas burnt.

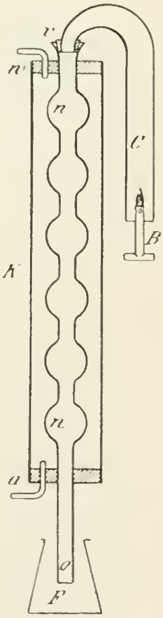

Fig. 105.

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FUEL ANALYSIS

By Professor F. FISCHER, Göttingen. English translation revised by
T. LEWIS BAILEY, Ph.D.

THE term *Fuel*, strictly speaking, is applied to the following substances:—Wood, peat, lignite, coal, and their products of carbonisation, viz., wood charcoal and coke.

The analysis of wood, considered as a fuel, is seldom carried out, and if done, is usually confined to the estimation of moisture. The moisture of freshly felled timber varies from 15 to 45 per cent.;[1] further investigation has no significance, as the composition of dry wood varies but little. The calorific power of dry wood is about 4500 calories.[2] Peat, on the other hand, varies considerably, not only in the amount of moisture it contains, but also in the percentage of ash and in the chemical composition of the peat substance proper;[3] consequently the calorific power is variable. Peat is, however, used as fuel in very few industries, so that its analysis is seldom required; when necessary, the same method that is employed for coal is adopted.

Sampling.—Before proceeding with the analysis, it is necessary to obtain an average sample, for if the sample be not representative, the whole analysis naturally becomes worthless. In taking the sample, it is to be borne in mind, that the composition of the coal of some pits is very variable, whereas, in other cases, the variation is only slight. For instance, in a piece of Deister coal, weighing 5 kilos, Fischer found the ash to vary from 4 to 31 per cent. in different portions of the sample. In twenty-four samples from the Unser Fritz mine, the ash varied only between the limits 1·1 and 7·8 per cent.[4] Stein[5] found considerable variations in the composition of coals from Saxony. It is to be noted, too, that the rough-hewn coal often contains a different

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[1] *Cf.* F. Fischer's *Taschenbuch f. Feuerungstechniker*, 5th ed., p. 57.

[2] *Z. angew. Chem.*, 1893, **6**, 575; 1899, **12**, 334.

[3] *Fischer's Jahresber.*, 1894, 7; *Stahl u. Eisen*, 1901, **21**, 749.

[4] *Ibid.*

[5] Stein, *Untersuchung der Steinkohlen Sachsens*, 1857; Fischer, *Chemische Technologie der Brennstoffe*, vol. i., p. 503.

amount of ash from the cobbles, so that, in sampling, relative proportions of each grade of the material must be taken.

As an example of sampling, suppose that an average sample of the fuel used for a boiler trial, extending over ten to twelve hours, is required. A shovelful is taken from each consecutive barrow-load, or from every second load, and put into a covered box; the coal is subsequently broken down, mixed over, spread out in the form of a square, and divided by the diagonals into four parts. Two opposite quarters are thrown out, the remaining two mixed, broken down further, again quartered, and so on, until only about 2 kilos (4 lbs.) remain. This sample is then bottled and sealed. For accurate work, it is advisable to prepare a second sample from the first half of the material thrown out, and to use this for an independent analysis. As there is danger of a loss of moisture during sampling, smaller samples, of about 50 g. each, are taken from time to time and put into weighed stoppered bottles, to serve for the moisture determination.

Preparation for analysis.—The samples are first coarsely crushed and well mixed; 200 g. are then finely powdered, care being taken that none of the more difficultly crushed portions are thrown out.

Moisture.—This determination must not be carried out in open vessels, as many fuels oxidise slowly in the air, on being warmed.[1] For technical purposes, 5 to 10 g. of the fuel are warmed between two watch-glasses, or in a covered crucible, for a couple of hours, at a temperature of 105° to 110°, in an air-bath, then allowed to cool in a desiccator, and subsequently weighed. In the case of the 50 g. samples, previously mentioned, the moisture is ascertained by weighing the stoppered bottles with their contents before and after drying.

An alternative method is to effect the drying over concentrated sulphuric acid, in a vacuum desiccator, for twenty-four hours.

Ash.—This estimation is especially necessary in the case of coal and coke. From 2 to 5 g. of the finely powdered sample, according to the probable quantity of ash present, are heated in a platinum dish. The heating must at first be gentle, and the temperature must be increased gradually, so as to prevent rapid formation of gas and consequent mechanical loss of ash, in the form of dust; finally, a moderate red heat is employed until the operation is complete. During the later stages, the ash is occasionally stirred with a platinum wire. The gradual heating is more especially advisable in the case of caking coal, a small flame being employed at first, best after about two hours' previous heating in an open dish, in an air-bath, at 120° to 150°; this prevents sintering of the coal.

Some kinds of coke, and also furnace clinker, are difficult to burn completely to ash, unless they are very finely powdered, and they

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[1] *Z. angew. Chem.*, 1899, **12**, 465 and 766.

require frequent stirring during the combustion. Excessive heating is to be avoided, owing to possible loss of alkalis.

G. Lunge's method of determining ash may be strongly recommended. A circular hole is cut in a piece of asbestos board and the crucible is placed in this, as shown in Fig. 106; the flame thus comes in contact with the lower part of the crucible only, and the fuel itself is in free contact with the air. If many ash determinations have to be carried out, shallow rectangular trays of platinum (Fig. 107) may be conveniently employed; samples of only 1 to 2 g. are taken, which are heated gradually in a muffle furnace (Fig. 108). In this way a number of determinations can be carried out simultaneously.

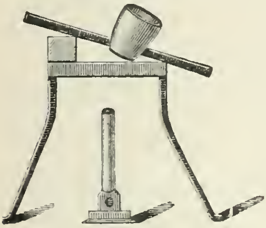
Fig. 106.

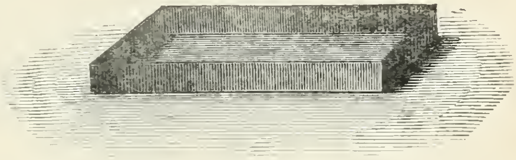
Fig. 107.

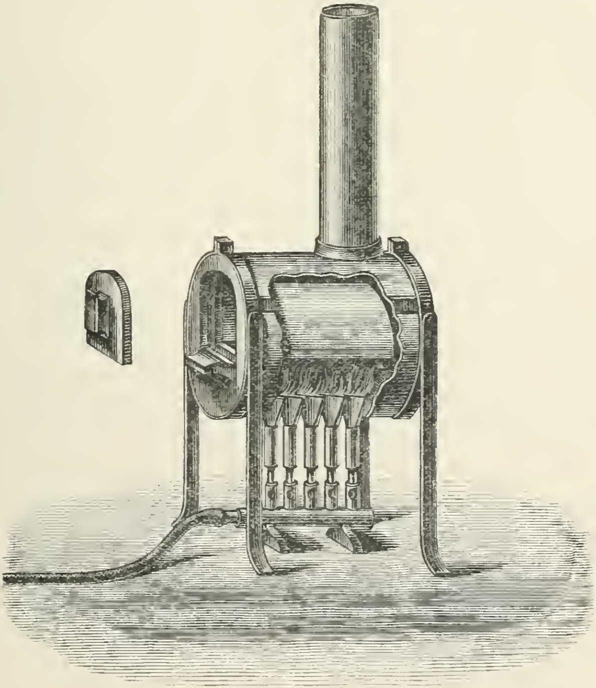
Fig. 108.

After weighing the ash, it may be further examined; an alkaline ash, or one which produces effervescence with hydrochloric acid, will attack acid refractory materials; the ash may also be tested for sulphates and phosphates, and its fusibility, etc., ascertained.

Residual Coke or Fixed Carbon.—From 1 to 1·5 g. of the sample is heated in a covered platinum crucible, placed on a platinum wire triangle. The heating is effected by a good Bunsen flame, the crucible being completely enveloped by the flame; the bottom of the crucible should be about 3 cm. above the top of the burner. Heating is continued until flame no longer issues from under the crucible lid.[1]

According to Constam and Rougeout,[2] the results obtained by this method are from 1 to 3 per cent. too high, and they give preference to the following method, due to Broockmann.[3] The sample is placed in a crucible, between 22 and 35 mm. deep, provided with a well-fitting cover, in the centre of which is a hole 2 mm. in diameter; the bottom of the crucible is placed about 6 cm. above the top of the burner, the total height of the flame above the burner exit being 18 cm. The heating is continued until there is no longer any flame burning at the hole in the crucible lid.

A modified form of Henrich's method[4] has been adopted in the United States, as the result of a report by a Special Committee on Coal Analysis.[5] An ordinary platinum crucible, supported by a platinum triangle, is used, placed 6 to 8 cm. above the top of the burner, and the heating is continued for seven minutes. The determination is made on the undried, finely powdered sample.

Gruner[6] recommends a short form of examination of coal, which consists in ascertaining the yield of coke (reckoned ash-free), and the percentage of moisture; the difference gives the amount of volatile matter given off on coking. He considers that those coals which give the smallest amount of coke have the lowest heat-producing value on combustion, a statement which is not altogether correct.

Von Jüptner's method[7] is similar; his method of calculation of the calorific power is open to criticism.

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[1] *Cf.* Fischer, *Technologie der Brennstoffe*, vol. i., p. 111; also, Muck, *Entwicklung der Steinkohlenchemie*, p. 18.

[2] *Glückauf*, 1906, **42**, 481; *J. Soc. Chem. Ind.*, 1906, **25**, 631.

[3] Muck, *Chemie der Steinkohle*, p. 32.

[4] *Z. anal. Chem.*, 1869, **8**, 133.

[5] *J. Amer. Chem. Soc.*, 1899, **21**, 1122; *cf.* also, Somermeier, *ibid.*, 1906, **22**, 1002.

[6] *Dingl. polyt. J.*, 1876, **219**, 178.

[7] *Die Bestimmung des Heizwertes von Brennmaterialien*, by H. von Jüptner, in *Sammlung chemisch-techn. Vorträge*, edited by Ahrens, vol. ii., pt. 12, 1898; cf. *Z. angew. Chem.*, 1901, **14**, 1260.

The appearance of the crust of coke, produced in the crucible from finely powdered coal, is differentiated as follows:—

Rough, fine-grained.	Black.	Porous all over or to near the edge	1. Sand-coal (long flame dry coal).
		Fritted hard, porous in centre only	2. Sintered sand-coal.
		Fritted hard all over	3. Sinter-coal (long flame fat coal).
	Grey and hard, with blistered appearance		4. Caking Sinter-coal.
Smooth, lustrous, and hard			5. Caking coal proper.

Schondorff[1] gives the following data as characteristic:—

Class of Coal.	Yield of Coke. Per cent.	Character of Coke.
1. Long flame dry coal	50 to 60	Pulverulent or sintered.
2. Long flame fat coal (gas coal)	60 to 68	Fused, but considerably fissured.
3. Fat coal proper (furnace coal)	68 to 74	Fused; tolerably dense.
4. Short flame fat coal (coking coal)	74 to 82	Fused; very dense; few fissures.
5. Poor anthracitic coal	82 to 90	Sintered or powdery.

In the case of caking coal, the increase in volume should be taken into consideration.

Sulphur.—Sulphur occurs in coal as iron pyrites; it is seldom combined with other metals. It is present also in the form of organic compounds[2] and as sulphates. The determination of the character and amount of these various compounds serves no useful purpose from a technical standpoint; the important factor to know, is the amount of sulphur present and the proportion which is detrimental to the process in which the fuel is to be used.

During the distillation of coal, either in gas retorts or in coke ovens, the sulphates are reduced to sulphides, pyrites forms ferrous sulphide, and oxide of iron may be converted into sulphide, by interaction with the organic sulphur compounds. How much of the sulphur passes off in the gas and how much remains in the coke can only be ascertained by direct experiment and analysis.

When the coal is to be used for ordinary firing, only the "volatile sulphur" need be considered, that is to say, the sulphur which passes off in the products of combustion as sulphur dioxide and partly as sulphur trioxide. Neither the sulphur remaining in the ash nor the total sulphur give any useful information. On the other hand, in the case of those smelting processes in which the fuel comes into direct contact with the material, as in black-ash furnaces, blast-furnaces, etc., the estimation of the total sulphur is necessary.

The estimation of Total Sulphur is usually carried out by Eschka's

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[1] *Z. f. Berg.-, Hutten-, und Salinenwesen*, 1875, 149.

[2] Cf. *Z. angew. Chem.*, 1899, **12**, 766.

method.[1] About 1 g. of the finely powdered sample is mixed, in a platinum crucible, with 2 g. of a mixture composed of two parts of well-calcined magnesia and one part of anhydrous sodium carbonate. The crucible, without the lid, is placed in a hole cut through an asbestos board (Fig. 106, p. 243), and is heated in such a way that the lower half only of the crucible attains a red heat. Heating is continued for about an hour, the mixture being frequently stirred with a thick platinum wire. As soon as the grey colour of the mixture has given place to a uniform yellowish, reddish, or brownish tint, the heating may be considered to be finished. After cooling, the crucible is placed in a beaker and covered with water; this is raised gradually to boiling, and extraction is completed by successive additions of water. Bromine water is then added until the liquid becomes slightly yellow, and the solution warmed to effect the oxidation of any sulphides present. The whole is then filtered, the filtrate acidified with hydrochloric acid, and barium chloride added to the boiling solution. From the amount of barium sulphate obtained, the sulphur is calculated in the usual way.

According to the proposal of Rothe,[2] the roasting of the mixture may be carried out in a porcelain crucible, placed in a muffle furnace. The duration of the operation may be shortened by carefully adding sodium peroxide, little by little, to the roasting mass, until oxidation is complete.

C. Sundström,[3] as also Pennock and Morton,[4] use sodium peroxide alone; Konek[5] determines the sulphuric acid, in the solution obtained in the estimation of the calorimetric value of fuel, by Parr's method (p. 256). A modification of this method is described by Schillbach.[6]

With the object of avoiding the possibility of error, from sulphur formed in the combustion of the gas used for heating, Brunck[7] has proposed a method for the determination of sulphur in coal, which consists in heating 1 g. of the sample, mixed with 2 g. of a mixture of 2 parts of cobalt oxide and 1 part of sodium carbonate, in a current of oxygen. The combustion is completed in fifteen minutes. The products of the oxidation are extracted with water, the cobalt oxide filtered off, and the sulphuric acid estimated gravimetrically. With certain coals, the oxide of cobalt may retain sulphur as a basic sulphate, which must be tested for and determined, if present.

The Volatile Sulphur can be ascertained by subtracting the sulphur of the ash from the total sulphur, or it may be determined directly, by combustion of the coal in a current of oxygen. This latter determination is carried out in the same way as an organic analysis, but a larger

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[1] *Z. anal. Chem.*, 1878, **17**, 497; *J. Soc. Chem. Ind*, 1889, **8**, 361.

[2] *Mitt. techn. Versuchsanst*, Berlin, 1891, 107.

[3] *J. Amer. Chem. Soc.*, 1903, **25**, 184.

[4] *Ibid.*, 1903, **25**, 1265.

[5] *Z. angew. Chem.*, 1903, **16**, 516.

[6] *Ibid.*, 1903, **16**, 1080.

[7] *Ibid.*, 1905, **18**, 1560.

weight of sample is necessary (0·8 to 1 g.), and the combustion tube should contain a short length of platinum clippings at *n* (Fig. 112), instead of the usual copper oxide. The sulphur dioxide and trioxide produced are passed into hydrogen peroxide, and the sulphuric acid thus produced is either precipitated as barium sulphate or is titrated with *N*/10 potassium hydroxide.

Arsenic has been found in certain samples of English coal and coke;[1] methods for its estimation have been described by Thorpe,[2] and by M'Gowan and Floris.[3]

Phosphorus.—The estimation of phosphorus is necessary only for metallurgical purposes. One to two g. of the ash are digested with concentrated hydrochloric acid, the whole taken to dryness, and the residue extracted with water containing a little hydrochloric acid. This solution, after the addition of nitric acid, is again taken almost to dryness and precipitated with ammonium nitro-molybdate in the usual manner.

Nitrogen.—This determination is not often required. In the Kjeldahl method,[4] 0·8 to 1 g. of the very finely powdered coal is mixed in a flask of well-annealed potash glass, with 1 g. of finely ground yellow mercuric oxide and 20 c.c. of concentrated sulphuric acid; the mixture is heated in a fume chamber for about an hour, on a hot plate, until the more energetic part of the reaction is past, and is kept subsequently at the boil for from one to two hours, on a wire gauze, until the solution is colourless. All classes of coal, even anthracite, dissolve in the time stated. After cooling, the contents of the flask are transferred to a second flask of about $\frac{3}{4}$ litre capacity, containing a little water, and standing in cold water; 120 to 140 c.c. of pure sodium hydroxide solution of sp. gr. 1·26 to 1·28 are added (made by dissolving about 310 g. of caustic soda sticks in water and making up to a litre) and 35 c.c. of a solution of yellow sodium sulphide, containing about 40 g. to the litre, together with a small piece of zinc, to prevent bumping during boiling. The whole is then distilled for from twenty to thirty minutes into a receiver containing 30 c.c. of *N*/20 sulphuric acid. By employing a tall distillation flask of considerable capacity, the introduction of a bulb between the flask and condenser, for the purpose of catching alkaline liquid mechanically carried from the flask, is rendered unnecessary. The sulphuric acid in the receiver is finally titrated with *N*/20 baryta water, or with *N*/10 sodium hydroxide solution, using rosolic acid as indicator.

According to investigations by Fischer,[5] the inconvenience of using sodium sulphide and mercury may be avoided as follows:—About 1 g.

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[1] *J. Soc. Chem. Ind.*, 1901, **20**, 437.

[2] *J. Chem. Soc.*, 1903, **83**, 969.

[3] *J. Soc. Chem. Ind.*, 1905, **24**, 265.

[4] Cf. *Z. anal. Chem.*, 1886, **25**, 314, and subsequent papers.

[5] *Fischer's Jahresber.*, 1894, 6.

of peat, powdered lignite, or very finely powdered coal, is boiled with 20 c.c. of concentrated sulphuric acid (free from nitrogen compounds), and 8 to 10 g. of potassium sulphate, using the same precautions as described above; decomposition is complete in about two hours, after which the ammonia may be distilled over and estimated as usual.

The determination of Carbon and of Hydrogen. — Since wood, in a finally divided condition, and more particularly peat, absorb moisture very readily, after having once been dried, the accurate weighing of such samples for ultimate analysis or for calorific power determinations is a matter of some difficulty. This difficulty, as well as the danger of error due to the oxidation of coal during drying (p. 242), may be avoided by weighing out 0·3 to 0·4 g. of very finely powdered coal, or about 0·5 g. of finely rasped air-dried wood, and compressing it in a cylindrical mould.

The kind of mould employed for the purpose is shown in Fig. 109. A steel ring *a* is clipped to the bottom plate *m*, by means of a hexagonal nut *n*. The sample is filled in, and is compressed by the small ram *s*; a strong copying-press, with iron base-plate, serves well for the purpose. The nut *n* is then unscrewed with the aid of a spanner, the inner ring *a* placed on a circular plate, and the sample pushed out by means of the ram *s*. The pressed cylindrical samples are then put into stoppered weighing bottles and dried at 105° to 110°.

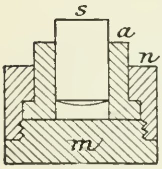

Fig. 109.

Towards the end of the operation, completion of the drying may be hastened by drawing air through the weighing bottle, or, in case several samples are being dried simultaneously, through the drying oven. To ensure that the samples are not broken down by the too rapid evolution of water-vapour during drying, the temperature is raised gradually to 105° to 108°; this precaution is especially necessary in the case of wood and peat. For the drying operation Fischer uses the apparatus shown in Fig. 110.[1] The cylindrical case is made of sheet copper and is 10 cm. in diameter; the lower portion is rounded as shown, and is provided with a brass tube *c*, to the lower end of which is attached a short calcium chloride tube, for drying the air to be admitted to the apparatus. The cover *t* is provided with an asbestos sheet on its under side. An asbestos shield, resting on a ring *r*, surrounds the whole, at a distance of about 5 mm. from the outside of the case. The gas tube *b*, is bent in the form of a ring and is pierced with four holes, thus providing four tiny gas flames.

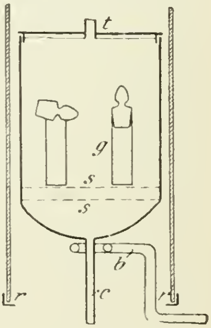

Fig. 110.

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[1] *Z. angew. Chemie*, 1894, 7, 19.

Two perforated trays *s*, ensure uniform heating of the samples contained in the weighing bottles *g*. The amount of gas required is extremely small.

The determination of the carbon and hydrogen, in the dried sample, is carried out in the same way as the ordinary ultimate analysis of organic compounds. Fischer[1] recommends the following modifications in the process. The two end-plates, *b* and *p*, of the combustion furnace (Fig. 111) are joined at their lower ends to the base-plate, and are connected above by the two iron rods *u*. The tiles *s* stand in a shallow channel running along each side of the furnace, and their upper ends rest against the rods *u*. The burner flame, protected from draughts by the side-plates *a*, is thus caused to pass completely round the combustion tube, which lies in a semicircular sheet-iron bed *o*. A combustion tube of hard glass is used; *aa* (Fig. 112) are two asbestos plugs, wrapped in very thin platinum foil, and between these is a layer of granular cupric oxide *n*, which in the case of coal containing much sulphur is replaced by a shorter layer of coarse lead chromate. After the introduction of the platinum boat *m*, containing the sample, the open end *u* of the tube is connected to an oxygen supply, and the calcium chloride tube *c*, fixed directly into the other end *w*.

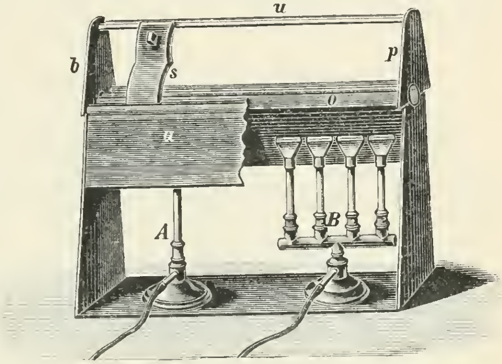

Fig. 111.

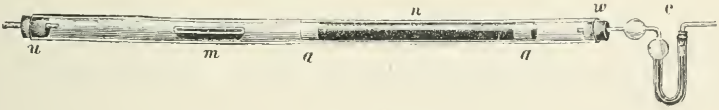

Fig. 112.

Before beginning the combustion proper, the tube is laid on the bed *o*, the tiles are placed against the rods *u* (Fig. 111), and the copper oxide is heated to redness by means of three or four flat-flame burners B (a portion of *a* is omitted in the figure so as to show the burners). A single burner suffices for heating the other portion of the tube. A current of air, washed by means of potassium hydroxide and dried by sulphuric acid, is first passed for about ten minutes, and the tube is then allowed to cool. The stopper *u* is then removed, the platinum boat containing the weighed sample introduced and the

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[1] *Chemische Technologie der Brennstoffe*, vol. i., p. 127.

stopper replaced. The calcium-chloride tube, etc., are attached, and the combustion is then carried out in the usual manner, in a current of oxygen.

Such modern improvements of the combustion process, as the use of electrically heated furnaces[1] and of Dennstedt's[2] simplified method of organic analysis, are of course applicable to the estimation of carbon and hydrogen in fuel.

The Determination of the Calorific Power of Fuel

The calorific power of fuels may be calculated from their elementary composition, or it may be determined by direct experiment. The formula of Dulong serves for the calculation; referred to liquid water at 0° C. as product of combustion, it is:—

$$[8100\,c + 34220\,(h - \tfrac{o}{8}) + 2500\,s] \div 100\,;$$

or, referred to water-vapour at 20° C., which is more practical,

$$[8100\,c + 28800\,(h - \tfrac{o}{8}) + 2500\,s - 600\,w] \div 100,$$

in which c, h, o, and s represent the percentages of carbon, hydrogen, oxygen, and sulphur respectively.

The value in B.T.U. is obtained by multiplying the value in calories by 3·97.

Dulong's formula gives fairly good results in some cases, whilst in others the results are from 2 to 6 per cent. out; in the case of wood, peat, and lignite especially, the results are considerably too low.[3] Many modifications of this formula have been proposed, but they are all only approximations. The true calorific power of fuels can only be reliably determined by means of direct calorimetric measurements. Numerous forms of apparatus have been proposed for this purpose,[4] of which those in which the combustion is effected in oxygen, either at atmospheric pressure or in the Berthelot bomb, are the most satisfactory.

Fischer's Calorimeter.—For carrying out the combustion at atmospheric pressure, Fischer[5] makes use of a combustion vessel of silver or of nickel-plated copper, which is clipped to the bottom of a nickel-plated copper cooling vessel B (Fig. 113), by means of three bent feet *f*. In the tube *d* of the cover is fixed a tube *e*, which is widened out into a plate at its lower end and carries a cylindrical vessel *p*, made of platinum or of nickel. Attached to the ring *l* is a small basket *s*, made of either platinum or nickel gauze, in which the

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[1] *Cf.* Blount, *Analyst*, 1905, **30**, 29; Morse and Taylor, *Amer. Chem. J.*, 1905, **33**, 591.

[2] *Ber.*, 1906, **39**, 1623.

[3] *Z. angew. Chem.*, 1893, **6**, 397 and 575; *Fischer's Jahresber.*, 1893, I.

[4] Fischer, *Chemische Technologie der Brennstoffe*, vol. i., pp. 129, 148, and 530.

[5] *Fischer's Jahresber.*, 1885, 1207. *Z. angew. Chem.*, 1892, **5**, 542; 1894, **7**, 19; 1901, **14**, 444.

sample is placed. If the sample is small, it is advisable to use a round basket. The opening in the bottom of the vessel *p* is covered with a piece of platinum gauze *c*, and underneath is a plate *v*. Oxygen is conducted into the apparatus through the glass tube *a*, and the products of combustion generated in *s* are carried downwards by the pressure of the oxygen, through the gauze *c*, and against the plate *v*, so that complete mixing and combustion is attained. The gases then pass through the outlet *i* into the flattened vessel *cc* (which may consist of a spiral tube), through the tube *g* and its glass extension *b*, to waste; or they may be collected in a gasholder, the oxygen being subsequently freed from carbon dioxide, and used for sulphur estimations and the like.

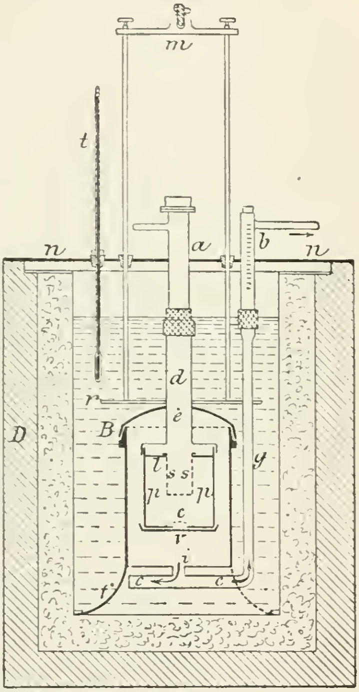

FIG. 113.

The cover *n* of the apparatus is made in two halves. One half is fastened down by means of a screw, and through it pass the rods of the stirrer *rm* and a thermometer *t*; the thermometer scale is graduated to read to $\frac{1}{20}°$, so that differences of $\frac{1}{100}°$ can be read by means of a cathetometer.

The space between B and D is loosely packed with dry swan's-down, and the joint between the edge of the copper vessel B and the wood case D is coated with shellac varnish, to prevent absorption of moisture. If the apparatus be kept dry when not in use, the heat loss is very small, amounting to 0·0025°, per degree difference of temperature, per minute. This value and the water equivalent of the apparatus are determined, either by the method of mixture,[1] or the water equivalent may be ascertained by weighing, thus :—

	Grams.	Sp. heat.	Cal.
Weight of containing-vessel with stirrer .	916·5	0·095 =	87·1
Weight of silver calorimeter . . .	278·4	0·056 =	15·6
Allowance for platinum extras, thermometer, etc. . . .			2·3
			105

The value found by means of water, in the above instance, was 112 cal.; it is evident, therefore, that a certain amount of heat is communi-

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[1] *Fischer's Jahresber.*, 1885, 1208.

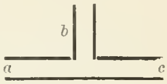
cated to the part of the apparatus surrounding B, so that about 5 cal. should be added, on an average, to the value obtained by weighing.

The ignition of the charge is effected in the usual way, by the introduction of a splinter of red-hot charcoal about 1·5 mg. in weight; the allowance necessary for this is 12 cal. The electrical ignition contrivance described on p. 215 may also be used; in this case about 2 mg. of gun-cotton or cotton wool are placed in the platinum spiral beforehand.

With some practice, it is quite easy to carry out a combustion so that the whole of the material is completely burnt; an examination of the gases passing from *b* is then unnecessary. There should be no deposit or smell noticeable on opening the calorimeter, after a combustion. Should it be deemed desirable, however, to examine the products of combustion, the gases escaping from *b* are passed through a bottle containing potassium hydroxide solution, so that the velocity and pressure of the exit gases may be observed; following this is a soda-lime tube 3 cm. in diameter and 20 to 25 cm. long, a similar tube containing calcium chloride, and then a combustion tube 15-20 cm. in length and containing a 4 cm. layer of copper oxide, placed between pieces of coarse platinum or nickel gauze. To the end of this tube a calcium chloride tube, 2·5 cm. in diameter, and a similar tube containing soda lime, are attached. From the increase in weight of the two latter tubes, the amount of the incompletely burnt gases can be determined.

The manipulation is as follows:—A compressed sample of the fuel is taken, by means of forceps, from the weighed drying bottle, the weight of the sample being ascertained by difference; this is placed in the small basket *s*, *p* is then fixed on to the end of *d*, the cover fixed firmly on to the calorimeter, as shown in Fig. 113, a small quantity of a mixture of melted caoutchouc and vaseline being used to make it tight. The calorimeter is then placed in B, the tube *a* connected up to the oxygen supply, the necessary quantity of water poured into B, the cover *n* laid on, the thermometer *t* inserted, and the temperature observed until constant. The oxygen supply is then gently turned on, a small piece of glowing charcoal thrown in through *a*, and the cap on *a* quickly replaced; at the same time the oxygen supply is increased. In a couple of seconds or so it will be seen that combustion has begun, and then oxygen is supplied, at such a rate, that about 2 litres pass in the course of half a minute. As the energy of the combustion slackens, the oxygen supply is reduced to about one-third. The combustion occupies only three-quarters of a minute. In the course of a further couple of minutes, if the calorimeter is of silver, or of from three to four minutes, if the calorimeter is of nickel, the thermometer should show a maximum reading, which indicates the completion of the experiment.

Fischer uses two oxygen gasometers, with at least half a metre water-pressure, for the combustion; these are connected to a glass T-piece, and thence to the calorimeter. Assuming *c* to be connected to the calorimeter, *a* and *b* are connected to the oxygen cylinders by rubber tubes provided with screw clips. The clip on *a* is arranged to allow of the passage of about 1 litre of oxygen in a quarter of a minute, and a second easily removable clip is used for completely cutting off the supply. On the tube connected to *b* is a screw clip, by means of which the oxygen supply can be readily increased, as soon as ignition has taken place. On the first sign of combustion the removable clip is taken off *a*, so that an excess of oxygen is at once available. When the vigour of the combustion shows signs of decreasing, *a* is again closed, and the combustion is finished by means of the supply through *b*. It is well to pass about 2 litres of air through the complete apparatus in half a minute before proceeding to a determination, so as to ascertain that all connections are sufficiently open. No mechanical loss, even in the case of peat, can occur if this test is satisfactory.



Fischer uses 1600 g. of water with this apparatus, so that the total calorimeter value is 1600+110=1710. The heat loss of the calorimeter for 1° temperature difference, per minute, is only 4 cal., if the packing be kept dry. As an experiment lasts scarcely three minutes, this correction is small, being only 15 to 20 cal. If the cooling water is 1° to 1°·2 below the temperature of the room, this correction may be neglected.

The following figures will serve as an example:—

Temperature rise of water at end of 1 minute	1°·2
„ „ 2 minutes	2°·5
„ „ 3 „	2°·9
„ „ 4 „	3°·0

The mean temperature for the individual minutes may be taken as:—

1 minute	0°·6	corresponding to	2·4 cal.
2 minutes	1°·8	„	7·2 „
3 „	2°·7	„	10·8 „
4 „	2°·9	„	11·6 „
			32·0 cal.

For technical purposes, therefore, intricate calculations are unnecessary; it is quite sufficient to take two-thirds of the temperature rise as a mean, in this case 2°; thus 2×4×4=32. The correction is usually considerably less than this.

The gases escape at a temperature 1° to 2° higher than that of the cooling water, according to the rapidity of the oxygen current; that is to say, about 4° warmer than the oxygen employed. If 3 to 4 litres of oxygen are used, the loss of heat from this source is about 6 cal., which is practically the same as the heat produced by the charcoal used for the ignition. These two corrections, therefore, practically neutralise each other.

The greater part of the water formed in the calorimeter is condensed. If the calorific power is referred to liquid water as product of combustion, 6·1 cal. must be added for every 10 mg. of water-vapour given off; but if calculated to water-vapour at 20°, then 6·1 cal. must be subtracted for every 10 mg. of water condensed. The amount of water condensed can be ascertained by drying the calorimeter externally, and weighing, after removing *a* and *b*; it is then washed out with distilled water, to remove any sulphuric acid that has been formed, dried by warming, and again weighed.

The Berthelot Bomb Calorimeter.[1]—The bomb (Fig. 114), consists of an iron tube, lined with platinum, to which a strong bottom 10 mm. thick and a cover of about 30 mm. thickness, are screwed and soldered. It has a capacity of about 250 c.c., and should be tested to 50 atmospheres. It is closed by the headpiece A, provided with a screw plug *a*.

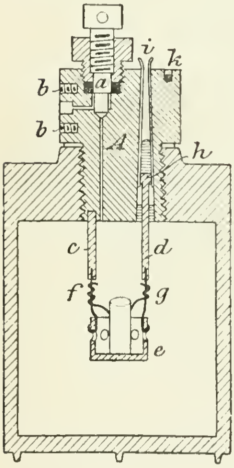


Fig. 114.

At *bb*, a flange (not shown) can be fastened on by screw bolts. An iron rod *c* is screwed into A, which also carries the insulated rod *d*, for electrical connection. Platinum wires *f* and *g*, of about 0·8 mm. thickness, are screwed and fastened firmly into *c* and *d* respectively; these carry a small fireclay tray *e*. The insulation of *d* is effected by a piece of thin-walled rubber tubing *i*, pushed over the thickened portion *h*, of the rod; by passing the tubing through the slightly conical hole in A, then pulling the tube and at the same time sharply pushing the rod *d*, a satisfactory fixing is effected. The lower portion of the rubber tubing is cut off, so that it shall extend about 1 cm. beyond the thickened portion of *d*, whilst at its upper end it projects somewhat beyond the hole. To prevent burning of the rubber inside the hole, its lower portion is packed with asbestos. The compressed sample of coal is put into electric connection with *f* and *g* by wrapping it round with platinum wire. Sheet lead is used to make the screw-plug and the headpiece quite gas tight. When the headpiece has been screwed into position, the apparatus is filled with oxygen. For this purpose connection is made with a cylinder of compressed oxygen, provided with a pressure gauge. In order to fill the bomb, the screw-plug *a* is eased to the extent of a full turn, and the tap of the

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[1] *Comptes rend.*, 1892, 115, 201.

oxygen cylinder carefully opened. As soon as the pressure in the bomb has reached 6 atmos., the cylinder tap is closed, and the oxygen is allowed to escape from the bomb, by somewhat slackening the flange bolts in *bb*; the escaping oxygen carries most of the nitrogen, originally contained in the bomb, with it. Oxygen is then again admitted and the pressure is allowed to reach 12 atmos., when the supply is cut off, the screw-plug closed, and the bomb placed in the calorimeter vessel, as shown in Fig. 115.

This consists of a covered metal vessel G, suspended in the vessel H, at a distance of about 2 cm. from its walls; G contains a litre of water. K is a thermometer, reading to $\frac{1}{100}^\circ$, and N a stirrer. The stirrer consists of a circular disc attached to a couple of rods and worked by means of a string passing through a ring, as shown in the figure. Wires pass from the mercury contacts *i* and *k* (Fig. 114), to a battery. When all is in readiness, the apparatus is allowed to stand until two successive readings of the thermometer, taken at an interval of five minutes, show that the temperature is constant. The electric circuit is then completed, and the ignition of the sample thus effected. Stirring of the water is continued until the temperature has attained a maximum and begins to fall. The initial and final temperatures are noted.

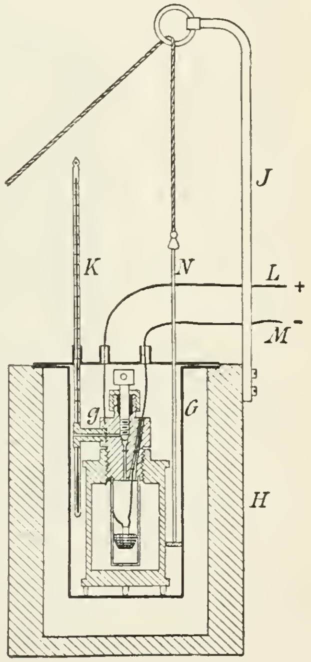

Fig. 115.

Kroecker[1] furnishes the upper portion of the bomb with two passages, capable of being absolutely closed. One is intended for the introduction of the oxygen, the other is continued inside, to the bottom of the bomb, by means of a platinum tube; this latter is intended for the removal of the gaseous products of combustion and the condensed water, after the combustion is finished. Both openings can be closed by plugs. In addition to these two passages is a third, through which an insulated platinum wire is passed.

Of other modifications of the Berthelot bomb the following may be mentioned :—

Scheurer-Kestner and Meunier-Dollfus[2] use a platinum-lined steel bomb. W. Hempel[3] makes use of the Berthelot principle, and inserts a platinum wire into the sample, for the purpose of electrical ignition.

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[1] *Z. angew. Chem.*, 1897, 10, 327; 1898, 11, 865; 1901, 14, 444.

[2] *Bull. Soc. Ind. Mulhouse*, 1891, 577.

[3] *Z. angew. Chem.*, 1892, 5, 389; 1896, 9, 486.

The *Mahler bomb*[1] is a cylinder of mild steel 8 mm. thick, and of about 650 c.c. capacity; it is nickel-plated on the outside and enamelled inside, so as to withstand the corrosive and oxidising action of the products of combustion. The shell narrows somewhat at the top, and the cover, which carries the tray for the sample, is screwed on the outside of this. The cover is provided with a lead ring, fitting into a groove in the edge of the bomb. The gas is admitted through a conical nickel-steel valve in the centre of the cover. The calorimeter itself is of thin brass, and the amount of water employed is 2·2 kilos, so that error due to evaporation is eliminated; the correction for loss of heat during the experiment is almost negligible.

The Mahler-Donkin[2] bomb calorimeter is constructed of non-corrosive metal, and is gold-plated inside.

Lunge[3] remarks that the Mahler bomb is costly, if one is to employ all necessary appurtenances. Including the delicate thermometer, stirrer, bomb, etc., the cost approaches £60, and accurate results can only be expected if the apparatus is used in a special room, of constant temperature. The use of highly compressed oxygen and the other operations entailed in connection with all bomb apparatus require considerable skill, so that the apparatus is, in his opinion, unsuitable for inexperienced workers.[4] One of the chief drawbacks is the liability of the enamel lining to injury, such injury not being repairable. Langbein[5] also points this out, and is in favour of lining the bomb with platinum.

Holman and Williams[6] replace the enamel lining of the Mahler bomb, by electroplating the inside with gold, and have also improved the methods of making the apparatus tight.

The Mahler bomb has been successfully used by J. Pfeiffer,[7] for the determination of sulphur in petroleum and other fuels, side by side with the estimation of the calorific value. From 2·0 to 2·5 g. are taken for the determinations, and the combustion is effected under a pressure of 30 atmos. of oxygen; the total sulphur remains in the bomb, after the combustion, in the form of sulphuric acid, and is determined gravimetrically.

Parr's Calorimeter.—In this apparatus the sample is burnt with sodium peroxide. A nickel-plated vessel A (Fig. 116), of about 2 litres capacity, serves as the calorimeter. This is placed inside a wooden vessel C, which itself stands in a similar vessel B. The two air-spaces, *a* and *b*, and the double cover G, containing an air-space *g*,

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[1] *Cf.* Mahler, *Études sur les Combustibles*, 1903; also, *J. Soc. Chem. Ind.*, 1892, **11**, 840.

[2] *Cf.* Dowson and Larter, *Producer Gas*, p. 221.

[3] *Z. angew. Chem.*, 1901, **14**, 794.

[4] Cf. *ibid.*, 1898, **11**, 865.

[5] *Ibid.*, 1900, **13**, 1235; 1901, **14**, 1260.

[6] *Cf.* Gill, *Gas and Fuel Analysis*, 1901, p. 57.

[7] *Bull. Soc. de Sciinte*, 1900, **8**, No. 6.

and the wood material of the vessels, provide sufficiently for all practical purposes, against loss of heat. The reaction vessel D (Fig. 117) consists of a strong nickel-plated brass cylinder, the ends of which are firmly screwed on, and provided with leather washers; it has a capacity of about 35 c.c. The base J rests on a conical support F, forming part of the inner vessel E; from the upper end of D passes the tube H, which extends right through the cover G, and is provided with a pulley P. A series of four small propeller blades, *hh*, is attached by spring clamps to D. D is rotated by means of a water turbine, and by employing a sufficiently high speed, the water can be kept in circulation through E in the direction of the arrows; a thorough mixing is thus produced, and an even temperature maintained. The blades *h* are so fixed as to cause the current to flow downwards next to the cylinder D and upwards outside E, when the rotation is right-handed. Inside the tube H (Fig. 117) is a narrower tube L, notched on one side and continued downwards to a conical valve K. By the action of a spiral spring M, connection with the interior of D is cut off, unless the tube L is depressed by pressure at N; any escape of gases, during combustion, is thus prevented. Ignition of the charge is brought about by dropping a red-hot piece of iron wire into L, then sharply depressing N, when the wire drops through K into D. A delicate thermometer, held in position by a thick rubber ring and reaching about half-way down the vessel A, is passed through a hole 8 to 9 mm. wide in the cover G. The double vessel B C is placed on a firm table, within reach of the necessary motive power. Two litres of water are poured into A before it is placed into position, so as to avoid water being splashed into C; for if the outer side of A or the inner portion of C should be moist this would ultimately produce an error in the results, owing to its evaporation. The temperature of the water should be about 2° below the temperature of the room. A is carefully set into C, and is then ready to receive the reaction vessel D.

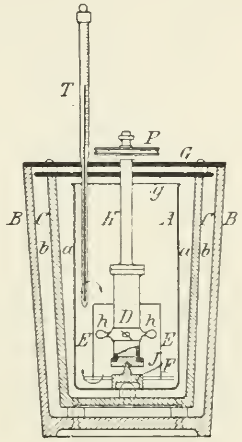

FIG. 116.

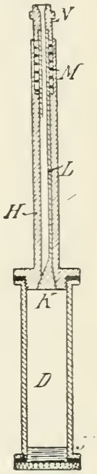

FIG. 117.

The latter is carefully dried internally and externally, which is best done by gently warming on a sand-bath or hot-plate, the base J is screwed on and tightened with a key. About 10 g. of sodium peroxide (passed through a sieve of 1 mm. mesh) are then introduced. This reagent is best kept in a wide-mouthed stoppered bottle, along with a small measuring vessel, supplied with the instrument; the measuring vessel, which holds 10 g. of the reagent, is made of nickel-plated brass, and is provided with a small handle.

After introducing the sodium peroxide into D, 0·5 to 1 g. of the coal sample, together with any other necessary reagents, is put in, the cover screwed on, and the whole well shaken, K being kept closed by an upward pressure of the finger on N, otherwise a small quantity of the mixture may be shaken into L. The vessel is then tapped, to bring the whole of the mixture to the bottom, the working of K tested to see that it acts smoothly, and the blades *h* clamped on; D is then placed inside A so that it rests on the conical peg at the bottom.

Lunge[1] recommends the following method for carrying out the determination:—

The coal to be tested is powdered, and should be passed through a wire sieve of 0·3 mm. mesh; in the case of hard coals and anthracite, a more finely divided sample should be used, which may be obtained by placing a piece of bolting cloth under the wire sieve. Lignite must be previously dried, for about an hour, at a temperature of 105° to 110°; exactly 1 g. of this substance is then weighed out and shaken into the reaction vessel, previously charged with the 10 g. of sieved sodium peroxide, after which the vessel is closed and shaken for one to two minutes, as described above. Bituminous coals do not require previous drying, unless the moisture exceeds 2 to 2½ per cent. In the case of coal, exactly 0·5 g. is weighed out, and to this is added exactly 0·5 g. of finely powdered pure tartaric acid; this mixture is then added to the usual 10 g. of the peroxide. The addition of potassium persulphate, which has been suggested as necessary for the combustion of hard coals and anthracite, is regarded by Lunge and Grossmann[2] as superfluous and as the source of discordant results.

The cover G having been placed in position, the pulley P is attached, and the thermometer inserted in the cover, as shown in the figure. The turbine is then set in motion so that the pulley revolves in the direction of the hands of a watch. A speed of about 150 revolutions per minute is kept up until the thermometer shows a constant temperature, which takes about three minutes; this temperature is noted, and the motor is kept running at the same speed till the conclusion of the experiment.

Ignition is effected by means of a piece of red-hot iron wire, 2·5 mm. in diameter and 10 mm. long; a piece of this size should weigh about 0·4 g., and the same piece can be used a good many times before

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[1] *Z. agnew. Chem.*, 1901, 14, 794 and 1270; 1903, 16, 911; 1905, 18, 1249.

[2] *Ibid.*, 1905, 18, 1249.

its weight falls much below 0·4 g. Experience has shown that soft iron is more suitable for the purpose than nickel, copper, silver, or platinum. It does not melt, as the first three of these do, forming peroxides, but it becomes covered, when first used, with a hard, black, adhesive coating of the magnetic oxide, which protects it for a considerable time. Using the above weight and at a temperature of, say 700°, the heat introduced by the iron amounts to $0·4 \times 0·12 \times 700 = 33·6$ calories, corresponding to a temperature rise in the calorimeter, of 0°·016. As the readings are carried out to 0°·005, a constant deduction, fixed at 0°·015 is made. The wire, held pointing downwards with a pair of bent tweezers, is heated to redness and dropped through N; N is then sharply depressed with the tweezers, so that the iron passes through K, without permitting any escape of gas through L. A hissing noise, lasting for several seconds, denotes the combustion of the charge, and the thermometer rises, at first rapidly, then more slowly; after about four or five minutes the maximum temperature is attained, which remains constant for about five minutes, when the reading is taken. The experiment is then finished. The motor is stopped, the thermometer, pulley, and cover are taken off, the vessel A, with contents, is taken out bodily, and the agitators *hh* are removed from D, which is taken to pieces and placed in a basin of warm water, so as to dissolve out the contents. On neutralising the solution so obtained, with hydrochloric acid, the presence of any unburnt fuel can be detected; should any be present, the results are worthless.

Calculation of results. The water value of the instrument was 123·5 g.; including the water, therefore, the total value is 2123·5 g. Of the heat $t'-t$ produced,—t' being the final and t the initial temperature of the calorimeter,—72·5 per cent. is regarded as due to the combustion proper, and 27·5 per cent. to the reaction of the products of combustion with the sodium peroxide and oxide. When 1 g. of the fuel is burnt, as is the case with lignite, the number of calories produced is thus $0·725 \times 2123·5\ (t'-t) = 1540\ (t'-t)$. It is simply necessary therefore to subtract 0°·015 from the recorded value, $t'-t$, on account of the heat introduced by the iron wire, and to multiply by 1540; the result gives the calorific power in centigrade units. With coal, only 0·5 g. is used, so that the recorded temperature difference is multiplied by $1540 \times 2 = 3080$. It is necessary first, however, to subtract the heating due to the combustion of 0·5 g. of tartaric acid, and that due to the iron; careful experiments have shown this to be 0°·832. If the sodium peroxide contains an excessive amount of moisture, as may be the case if a considerable quantity of peroxide is kept and frequently opened for use, the results will come out too high. It is then necessary to make a blank test, using 0·5 g. of tartaric acid, and about two-thirds of a measure (about 7 g.) of sodium peroxide. If the calorimeter temperature rises more than 0°·832, it will be necessary, in future use of this stock, to take such extra rise into consideration, by allowing 0°·15 for every 0°·1 excess rise obtained in the blank experiment (0°·15 being, of course, the allowance for a full measure of 10 g. of peroxide).

Parr's method of determining calorific power is more convenient, cheaper, and far simpler in manipulation, than any of the processes involving the use of a bomb, but it has certain obvious defects. In the first place, the combustion may be either too violent or incomplete, if the proportion of added materials is not appropriately adjusted; secondly, the heat generated by the absorption of the water and carbon dioxide, formed in the combustion by the sodium peroxide, has to be determined empirically for each instrument; and thirdly, the value of the coefficients given above does not hold for all kinds of coal, and still less for other fuels, such as lignite, petroleum, etc. These points have been specially investigated by Lunge and Offerhaus,[1] and by Lunge and Grossmann.[2] The latter conclude that the method is unreliable for coals having a calorific value less than 7500 cals. For coals having a higher calorific value, the method is of practical value, under the conditions given above. Both the coal and the sodium peroxide must be finely powdered and intimately mixed, and the peroxide must be of good quality. The heat value of the tartaric acid, together with that of the ignition wire, to be subtracted from $t' - t$, should be 0°·832, as given above, instead of 0°·85 previously accepted, and the coefficient should be 1540 as stated, in place of 1550 as formerly used. The latter value holds, of course, only for a calorimeter of the water value 2123·5 when charged.

Langbein[3] discards Parr's process as altogether unreliable, but this conclusion is not justified.

Lewis Thompson's Calorimeter, in which the fuel is oxidised by a mixture of potassium chlorate and nitre, is largely used for technical work. The determinations can be made very rapidly, and although the readings necessitate an empirical correction, the results are sufficiently accurate for many practical purposes.

The apparatus (Fig. 118) consists of a narrow copper cylinder or furnace B, a wider copper cylinder F, with small perforations round the base, and provided with a long narrow tube terminating in a tap and a glass calorimeter vessel A, graduated for a content of 2000 g. and of 29,010 grains. F is supported by the base C, in which it is held by the springs E; D is a socket to carry the furnace B.

The determination is made as follows:—2 g. of an average sample of the fuel, finely ground and sieved, are thoroughly mixed with about 20 to 24 g. of a well-dried mixture of three parts of potassium chlorate and one part of nitre; this is shaken down into the furnace, previously placed in the socket D, and ignited by a short fuse, consisting of a piece

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[1] *Z. angew. Chem.*, 1903, **16**, 911. [2] *Ibid.*, 1905, **18**, 1249. [3] *Ibid.*, 1903, **16**, 1075.

of ordinary wick soaked in potassium nitrate solution and subsequently dried, the end of the wick being embedded in the mixture. The cover F is then immediately fixed over the furnace, with the tap closed and the whole lifted and placed in A, previously charged with 2000 g. of water. Combustion soon commences and proceeds rapidly: the gases generated pass out through the holes in the base of the cover, and rise through the water. When the combustion is ended, which should occupy about two minutes, the tap on F is opened and the contents of the furnace thoroughly mixed with the water, by using the cover as a stirrer. The increase of temperature is read to within 0·05. The initial temperature of the water in A should be from 3° to 4° below the temperature of the room.

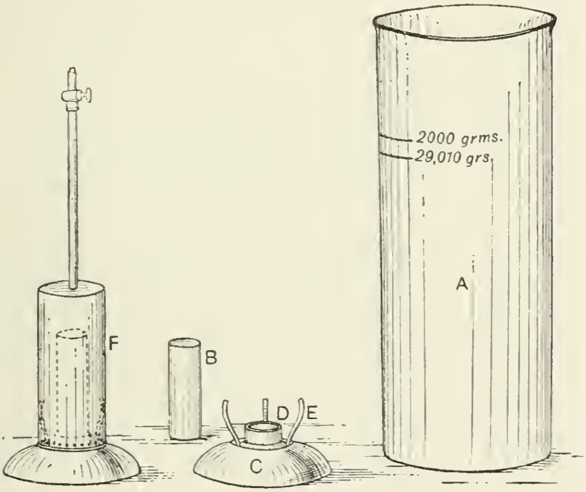

FIG. 118.

As the result of experiment, it has been shown that the average total of loss of heat in using the apparatus, due to that carried off by the escaping gases, that taken up by the apparatus itself, and that absorbed by the added salts and the products of combustion, is about one-tenth of the total, and this empirical correction is added to the observed rise of temperature, in each determination.

By taking 30 grains of fuel and placing 29,010 grains of water in A, the evaporative power, in British units, is obtained directly, if the temperature change is measured in Fahrenheit degrees, since the latent heat of vaporisation of water is 967 B.T.U. and 967 × 30 = 29,010 grains.

J. W. Thomas[1] has given a considerable amount of information regarding the capabilities of the Lewis Thompson calorimeter, and has

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[1] *Chem. News* 1881. 34, 135.

shown that the more bituminous a coal is, the better are the results; he does not appear, however, to have estimated the unburnt coal, of which there is frequently a considerable amount. W. Thomson[1] has pointed out most of the objections to the instrument. Scheurer-Kestner[2] has compared it with a Favre and Silbermann's calorimeter, and states that with 15 per cent. addition for losses, the results agree within a maximum of 4 per cent.

W. Thomson's Calorimeter[3] in some respects resembles the preceding, but combustion is carried out by means of oxygen, and the escaping gases, during their passage through the water, are baffled by a series of gauze rings. The addition of similar rings on the combustion chamber of the Lewis Thompson apparatus is of distinct advantage when using that apparatus.[4]

An improved form of the Thomson calorimeter has been devised by Gray,[5] in which the gauze baffles are replaced by thin perforated brass discs, and which is provided with an arrangement for the electrical ignition of the coal.

Rosenhain[6] has also modified the Thomson calorimeter in the details of construction, to render it more accurate for technical work, including its application to the calorimetry of volatile liquids.

Darling[7] has described an easily made apparatus, similar in principle to that of W. Thomson, but providing more intimate contact of the products of combustion with the cooling water.

The comparative value of the results obtained by the Lewis Thompson, the William Thomson, the Fischer, and the Mahler calorimeters, has been studied independently by Brame and Cowan,[8] and by Gray and Robertson.[9] These authors agree, that in order to obtain accurate results, a bomb calorimeter should always be employed. The only objection to its use is that of expense; at the same time it is not an instrument suited to the more expeditious requirements of chemical or of engineering works. The results obtained with the other calorimeters specified are always too low, owing to the difficulty of effecting complete combustion. Brame and Cowan state that the amount of unburnt coal should always be determined, in using the Lewis Thompson calorimeter; it then gives fair comparative results for bituminous coals. They found the calorific value from 1·8 to 6·2 per cent. lower than with the Mahler bomb; Gray and Robertson obtained

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[1] *J. Soc. Chem. Ind.*, 1886, **5**, 581.

[2] *Bull. Soc. Ind. Mulhouse*, 1888, 506.

[3] *J. Soc. Chem. Ind.*, 1886, **5**, 581.

[4] Brame and Cowan, *ibid.*, 1903, **22**, 1231.

[5] *Ibid.*, 1906, **25**, 409.

[6] *Phil. Mag.*, 1902 [iv.], 457; *J. Soc. Chem. Ind.*, 1906, **25**, 239.

[7] *Engineering*, 1902, 801; *J. Soc. Chem. Ind.*, 1902, **21**, 927.

[8] *J. Soc. Chem. Ind.*, 1903, **22**, 1230.

[9] *Ibid.*, 1904, **23**, 704.

results from 0·9 to 13·0 per cent. lower. The results obtained by Brame and Cowan with the Fischer calorimeter were from 2·6 to 5·7 per cent. lower than with the Mahler calorimeter; the results were concordant with the same coal. With the W. Thomson calorimeter the results were from 1·8 to 6·9 per cent. lower than with the bomb; the comparative values found by Gray and Robertson were from 0·7 to 2·9 per cent. lower.

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MANUFACTURE OF SULPHUROUS ACID, NITRIC ACID, AND SULPHURIC ACID

By Professor G. LUNGE; translated by JAMES T. CONROY, B.Sc., Ph.D.

SULPHUROUS ACID

FORMERLY sulphurous acid was produced almost entirely for conversion into vitriol by the lead-chamber process; to-day it is made in considerable quantity in connection with the sulphite-cellulose industry, and to a lesser extent for conversion into liquid sulphur dioxide. On this account it is accorded separate treatment.

RAW MATERIALS

I. SULPHUR (NATIVE SULPHUR)

Sicilian native sulphur is shipped in the form of blocks, each weighing from 28 to 30 kilos; owing to the friable nature of the sulphur, these blocks are usually shattered during transport into lumps of varying size and to some extent to powder. The best quality ("firsts," "prima Lercara" or "prima Licata"), consists of large, shining pieces of amber-yellow colour. The second quality ("seconds," "seconda vantaggiata") is also of a good yellow colour, but not quite so brilliant in appearance. The bulk appears in commerce as a third quality ("thirds," "terza vantaggiata"); its colour is dull and not pure yellow. Nevertheless the ash is frequently as low as ½ per cent., and seldom exceeds 2 per cent.; in exceptional cases it may rise to 4 per cent. or more. The fourth grade is of a greyish-yellow colour, and may contain up to 25 per cent. of earthy matter. "Zolfo ventilato" is sulphur which has been ground, separated by an air blast, and sieved.

Commercial Sicilian sulphur contains only very small quantities of volatile matter and of bitumen, and generally is free from, or contains only traces of, arsenic and selenium. The sulphur from the Solfatara at Naples, which Phipson found to contain 11·162 per cent. of arsenic and 0·164 per cent. of selenium, is of no importance as a commercial product.

The *degree of fineness* of ground sulphur must be determined when the sulphur is intended for application in vine culture to destroy the grape-disease *Oïdium*. This examination is effected by means of Chancel's *sulphurimeter*, shown in Fig. 119. The sulphurimeter consists of a cylindrical glass tube, 23 cm. long and 15 mm. diameter, sealed below, fitted with a glass stopper above, and graduated from the bottom upwards into 100 degrees. Each degree equals ¼ c.c.; the 100 degrees (25 c.c.) occupy a length of 100 mm. The ground sulphur is shaken with ether in the tube, and allowed to settle, when it forms a layer the height of which bears a relationship to the fineness of the grinding. The sulphur to be examined is first passed through a sieve of 1 mm. mesh, in order to break down the lumps formed during storage. Five g. of the sieved sulphur are placed in the tube, which is then half-filled with anhydrous ether as nearly as possible at a temperature of 17°·5. The sieved sulphur in the tube is broken down still further by thorough shaking, after which ether is added until the level stands 1 c.c. over the 100th division; the whole is again well shaken and the tube then fixed in a vertical position. When the sulphur layer has come to rest, its position on the scale is read off; the reading gives the fineness in "Chancel degrees." As a rule, ground sulphur shows 50° to 55°, finer qualities 70° to 75°, Zolfo ventilato 90° to 95°. For use in viniculture, a minimum of 60° and frequently of 75° Chancel is demanded.

Fig. 119.

According to H. Fresenius and P. Beck,[1] the dimensions of the sulphurimeter are of importance and must be exact; they recommend the instrument made by J. Greiner, Munich. This differs in its dimensions from the French instrument described above; the length of the tube to division 100 is 175 mm., the length of the straight portion between 10° and 100° is 154 mm., and the internal diameter 12·68 mm. The ether employed should be distilled over sodium, and all disturbance should be avoided after the shaking, the instrument being immediately clamped in a stand and immersed in water at 17°·5.

It may further be necessary to determine whether the fine sulphur intended for vine-dusting is really flowers of sulphur, or whether it consists of a mixture of ground sulphur with flowers of sulphur. This is best done by microscopic examination, the ground sulphur being distinguished by its crystalline appearance from the partially amorphous flowers of sulphur. The method is not, however, absolutely trustworthy, since flowers of sulphur change in course of time almost completely into the crystalline condition (Alpha sulphur). The partial insolubility of

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[1] *Z. anal. Chem.*, 1903, **42**, 21.

flowers of sulphur in carbon bisulphide may also be employed as a qualitative test, but with old samples the percentage of insoluble sulphur may occasionally be very slight. This reaction cannot be applied as a quantitative method, since the ratio between soluble and insoluble sulphur varies considerably even in freshly prepared flowers of sulphur.

Opinions differ very considerably as to whether crude sulphur or flowers of sulphur is the more efficient in viniculture. H. Fresenius and Beck recommend the former, maintaining that the crystalline ground sulphur adheres more firmly to the leaves than does the amorphous variety. In France, on the other hand, the latter form is preferred, owing to its finer state of division, as compared with the ground sulphur (which is frequently employed on account of its cheapness), and also because of the very active destructive action of the adhering acid on the *oïdium.*

The chemical examination of native sulphur includes the following determinations :—

1. **Ash.**—This is determined by burning off about 10 g. of sulphur in a tared porcelain crucible and weighing the residue.

2. **Moisture.**—In the case of lump sulphur this determination is frequently unnecessary, but it should be made if adulteration by spraying is suspected, or if the sulphur has been exposed to rain. The estimation is, however, always misleading, owing, on the one hand, to the difficulty of obtaining a genuine average sample, and on the other hand to the loss of moisture which almost inevitably occurs in breaking down the sample to suitable fineness for laboratory work. The sample should not be crushed further than to a coarse powder, and this should be done as speedily as possible. At least 100 g. should be taken for the estimation. In the case of ground sulphur, it is of course much easier to obtain an average and more finely divided sample. According to Fresenius and Beck, the drying operation should only occupy a short time and the temperature should not exceed 70°.

Difficulties in the moisture determination arising from the presence of gypsum have been experienced by F. B. Carpenter[1] in the examination of Mexican sulphur. He consequently recommends making the estimation by drying the sample *in vacuo* over sulphuric acid. A portion of the sample is freed from gypsum by boiling with dilute sulphuric acid, the residue dried and weighed, and the contained sulphur estimated, either by burning-off or by solution in carbon bisulphide (cf. *infra*).

3. **Bituminous substances.**—Any appreciable quantity is evidenced by the bad colour of the sulphur, but in most commercial sulphurs the amount present is too small to render a determination necessary.

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[1] *J. Soc. Chem. Ind.*, 1902, **21**, 832.

Sulphur recovered from gas residuals is, however, frequently quite black from the presence of this impurity.

H. Fresenius and Beck drive off the sulphur by heating to slightly over 200°, weigh the residue, ignite for ash and re-weigh, and regard the difference between the two weighings as representing the organic matter present.

4. **Arsenic.**—This impurity may occasionally occur in very minute quantity in Sicilian sulphur, to a greater extent in the Solfatara sulphur (see p. 264), and especially in sulphur recovered from pyrites or from alkali-waste. The arsenic may be present either as arsenious sulphide, As_2S_3, or as arsenious oxide, As_2O_3; exceptionally also as calcium or iron arsenite. J. T. Conroy (private communication) finds the sulphur recovered from alkali-waste by the Chance-Claus process particularly free from arsenic; tested by the Hager method, only very minute and doubtful traces are indicated. Sulphur recovered from pyrites does not show such freedom.

For a qualitative examination for arsenic, Hager's method[1] may be employed. It is carried out by shaking 1 g. of sulphur with 15 drops of ammonium hydroxide and 2 c.c. of water, filtering after half an hour, and adding to the filtrate contained in a test-tube 30 drops of hydrochloric acid and 15 drops of a solution of oxalic acid. A strip of clean brass is then placed in the solution and this is warmed to a temperature of 60° to 100°; in the presence of arsenic an iron-coloured to black film forms immediately on the brass. A blank test should always be made with the reagents used, and to ensure uniformity of temperature it is advantageous to heat the two test-tubes side by side, in a beaker of water.

Sulphide and oxide of arsenic may be extracted by digesting the sulphur with dilute ammonia at 70° to 80°; they remain behind on evaporating the ammoniacal extract. It is better, however, to add excess of hydrochloric acid to the ammoniacal extract and then precipitate by saturation with sulphuretted hydrogen; any arsenic originally present as As_2S_3 naturally comes down before passing in the gas. The arsenic present is best estimated by Schäppi's method,[2] which consists in exactly neutralising the ammoniacal solution with nitric acid, diluting, and then titrating with $N/10$ silver nitrate solution, using as indicator neutral potassium chromate, which is coloured brown by a drop of the solution after all the arsenic has been precipitated.

The salts of arsenious acid remain in the insoluble residue on extracting sulphur with carbon bisulphide; this residue must be digested with aqua regia and examined for arsenic in the usual manner, as is described more fully under "Sulphuric Acid."

5. **Selenium** may be detected by oxidising the sulphur, best by

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[1] *Pharm. Centr.*, 1884, 265 and 443.

[2] *Chem. Ind.*, 1881, 4, 409.

deflagrating with nitre; on dissolving the melt in hydrochloric acid and treating with sulphurous acid, selenium will, if present, be precipitated as a red powder.

In America, according to Reed,[1] the examination for selenium is carried out as follows:—0·5 g. of the sulphur is boiled with a solution of 0·5 g. potassium cyanide in 5 c.c. of water, the solution filtered, and the filtrate acidified with hydrochloric acid; after standing for an hour no red coloration due to selenium should result. A pale yellow coloration, due to perthiocyanic acid, may be neglected. The test is made still more sensitive by boiling 1 g. of the sulphur for an hour with a solution of 2 g. of potassium cyanide, then adding a further 0·5 g. potassium cyanide and continuing the boiling for half an hour. Any iron present will, of course, react with the thiocyanate formed.

6. Determination of Sulphur.—Macagno[2] recommends the direct method of extraction with carbon bisulphide, and has calculated a table for this purpose. The method has been recently investigated by Pfeiffer[3] and the specific gravities involved determined with considerable exactitude. To estimate sulphur by this process, a weighed quantity of the powdered sample is shaken in a well-stoppered bottle with at least four times its weight of pure carbon bisulphide, accurately weighed, and the specific gravity of a clear sample determined at a known temperature (+15° C. and higher).

The specific gravity thus determined is if necessary reduced to that at 15° C. by means of the formula:

$$\text{Specific gravity at } 15^\circ = \text{spec. grav. at } t^\circ \times \frac{1 + at + bt^2 + \cdot\ \cdot}{1 + a \times 15 + b \times 15^2}$$

where $a = 0{\cdot}0011398$ and $b = 0{\cdot}000001370$.

The percentage of pure sulphur in the sample examined is deduced from the formula:

$$\%\,\text{S} = \frac{a \times b}{c},$$

where—

a = the weight of sulphur dissolved by 100 g. carbon bisulphide, according to the following table,

b = the weight of carbon bisulphide used in the extraction,

c = the weight of substance.

For an approximate estimation, Marcilli[4] places 5 g. of the sample in a Chancel tube (Fig. 119, p. 265), fills the tube with carbon bisulphide, and, after inserting the stopper, shakes well and allows to settle; the volume of the undissolved portion is then read off.

Ceruti[5] uses aniline warmed to 75 as a solvent.

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[1] *Chem. Zeit. Rep.*, 1897, **21**, 252.

[2] *Chem. News*, 1881, **43**, 192.

[3] *Z. anorg. Chem.*, 1897, **15**, 194; also, P. Fuchs, *Z. angew. Chem.*, 1898, **11**, 1189.

[4] *Z. angew. Chem.*, 1906, **19**, 99.

[5] *Chem. Centr.*, 1904, **II.**, 615.

Specific gravities of solutions of Sulphur in Carbon Bisulphide with the corresponding weights of Sulphur dissolved by 100 parts by weight of pure Carbon Bisulphide at 15° C., compared with Water at 4° C.

Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.
1·2708	0·0	1·2999	6·4	1·3263	12·8	1·3507	19·2
1·2717	0·2	1·3007	6·6	1·3271	13·0	1·3514	19·4
1·2726	0·4	1·3016	6·8	1·3279	13·2	1·3521	19·6
1·2736	0·6	1·3024	7·0	1·3287	13·4	1·3529	19·8
1·2745	0·8	1·3032	7·2	1·3295	13·6	1·3536	20·0
1·2754	1·0	1·3041	7·4	1·3303	13·8	1·3543	20·2
1·2763	1·2	1·3050	7·6	1·3311	14·0	1·3550	20·4
1·2772	1·4	1·3058	7·8	1·3319	14·2	1·3557	20·6
1·2782	1·6	1·3066	8·0	1·3326	14·4	1·3564	20·8
1·2791	1·8	1·3074	8·2	1·3334	14·6	1·3571	21·0
1·2800	2·0	1·3083	8·4	1·3342	14·8	1·3577	21·2
1·2809	2·2	1·3091	8·6	1·3350	15·0	1·3584	21·4
1·2819	2·4	1·3100	8·8	1·3357	15·2	1·3591	21·6
1·2828	2·6	1·3108	9·0	1·3365	15·4	1·3598	21·8
1·2838	2·8	1·3116	9·2	1·3373	15·6	1·3605	22·0
1·2847	3·0	1·3125	9·4	1·3380	15·8	1·3612	22·2
1·2856	3·2	1·3133	9·6	1·3388	16·0	1·3619	22·4
1·2866	3·4	1·3142	9·8	1·3396	16·2	1·3626	22·6
1·2875	3·6	1·3150	10·0	1·3403	16·4	1·3633	22·8
1·2885	3·8	1·3158	10·2	1·3411	16·6	1·3640	23·0
1·2894	4·0	1·3166	10·4	1·3418	16·8	1·3646	23·2
1·2903	4·2	1·3174	10·6	1·3426	17·0	1·3653	23·4
1·2912	4·4	1·3182	10·8	1·3433	17·2	1·3660	23·6
1·2920	4·6	1·3190	11·0	1·3441	17·4	1·3667	23·8
1·2929	4·8	1·3199	11·2	1·3448	17·6	1·3674	24·0
1·2938	5·0	1·3207	11·4	1·3456	17·8	1·3681	24·2
1·2947	5·2	1·3215	11·6	1·3463	18·0	1·3688	24·4
1·2956	5·4	1·3223	11·8	1·3470	18·2	1·3395	24·6
1·2964	5·6	1·3231	12·0	1·3478	18·4	1·3702	24·8
1·2973	5·8	1·3239	12·2	1·3485	18·6	1·3709	25·0
1·2982	6·0	1·3247	12·4	1·3492	18·8	...	...
1·2990	6·2	1·3255	12·6	1·3500	19·0	...	...

In regard to the examination of refined sulphur—

Roll sulphur is generally to all intents chemically pure; it may be examined for ash, arsenic, and selenium (see p. 266).

Flowers of sulphur are not quite so pure; if not carefully washed, they are especially liable to contain free acid, more particularly sulphurous acid, sulphuric acid, and also thiosulphuric acid, which may be tested for by the usual methods. If intended for use in the manufacture of fireworks, the sulphur must be free from all trace of acidity. According to determinations made by Janda,[1] the residue on ignition amounted to 0·063 per cent. as an average of thirty samples, the maximum value being 0·283 per cent. The solubility in boiling sodium hydroxide solution of 1·2 sp. gr. led to a mean value of 98·04 per cent., with a maximum of 99·99 per cent., and a

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[1] *Jahresber. der chem. Tech.*, 1897, 421.

minimum of 88 per cent.; in one case, however, only 68 per cent. was dissolved.

According to Domergue,[1] only those products should be classed as "flowers of sulphur" which, when fresh, contain at least 33 per cent. insoluble in carbon bisulphide.

II. SULPHUR FROM GAS RESIDUALS

The spent purifying materials from gasworks frequently contain over 50 per cent. of free sulphur.[2] They are first freed from ammonium salts by extraction with water, and then subjected to a special treatment for the recovery of cyanogen compounds. The residue remaining after this treatment forms a valuable raw material for the production of sulphurous acid. It consists essentially of free sulphur and oxide of iron admixed with sawdust, tarry substances, etc., and may also contain varying quantities of lime, etc. Any lime present will, on burning, fix part of the sulphur, and on this account a method of analysis is adopted which takes account of available sulphur only.[3] The spent oxide is burnt by the aid of platinised asbestos, the resulting gases are passed into a solution of potassium hydroxide and potassium hypobromite, and the sulphuric acid contained in the resulting solution estimated by precipitation with barium chloride.

The burning is effected in a combustion tube, 60 cm. in length (Fig. 120), narrowed at *a*, and drawn out at one end into a downwardly directed and not too thin narrower piece 10 cm. long. A layer of platinised asbestos, 20 to 25 cm. long, is placed between *a* and *b*, and 7 to 10 cm. behind this a porcelain boat containing about 0·4 g. of the sulphur. The free end of the tube is connected at *k* with a gasholder containing oxygen. Two 14 cm. high bulb U-tubes *c* and *d* and the tube *e*, filled with glass wool, are employed for absorbing the evolved gases. They are charged with a solution prepared by dissolving 180 g. of potassium hydroxide (purified from sulphate by alcohol) in water,

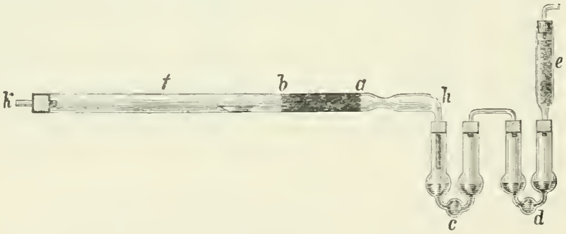

FIG. 120.

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[1] *Chem. Zeit. Rep.*, 1905, **29**, 19.

[2] The examination of these residuals for their more important constituents will be described in the section on Gas Manufacture, Vol. II.

[3] Zulkowsky, *Dingl. polyt. J.*, 1881, **241**, 52.

adding to this 100 g. of bromine drop by drop, cooling as required, and diluting to 1 litre; thirty c.c. of this solution are sufficient for the estimation of 0·5 g. sulphur. The glass wool in the tube *e* should also be moistened with the solution.

A current of moist oxygen is passed through the tube, and the portion between *a* and *b* heated to redness; the boat is then pushed in and the heating extended from right to left, until finally the tube is heated to the point *f*. The current of gas must be much stronger than that employed in ordinary organic combustions, in order to prevent sulphur from passing away unburnt; on the other hand, it must not be so strong that the sulphur dioxide escapes unabsorbed. Any deposit formed at *h* must be driven forward by means of a Bunsen burner; the combustion is complete when such deposit ceases to form, and this is usually the case after one hour. The absorbing vessels are then removed, emptied, and washed out; any sulphuric acid remaining in the tube at *h* is recovered by repeatedly drawing up water by suction applied at *k*. The solutions and washings are combined, hydrochloric acid added in sufficient excess to neutralise the alkali and decompose the hypobromite, the whole heated and if necessary concentrated, and the sulphuric acid precipitated as barium sulphate by addition of a hot solution of barium chloride.

This method is also applicable to the determination of available sulphur in pyrites; in this case the platinised asbestos is omitted, and the combustion tube, drawn out and bent round as above, need not be more than 40 cm. long.

Hydrogen peroxide may be used with advantage instead of potassium hypobromite solution, titration of the sulphuric acid by standard alkali being in this case substituted for the gravimetric determination. Allowance must, of course, be made for any acidity in the hydrogen peroxide employed. This modification is much more rapid than Zulkowsky's method, and does away with the necessity of employing absolutely sulphate-free potassium hydroxide. The reaction is simple:

$$H_2O_2 + SO_2 = H_2SO_4.$$

Similar methods, generally intended for the estimation of available sulphur in pyrites, have frequently been recommended; these are described below.

The estimation of the sulphur by oxidation with hydrogen peroxide always gives too high results, and some tar is also dissolved.

Pfeiffer[1] burns 1 g. of the sample in a bottle filled with oxygen, on the bottom of which a solution of sodium hydroxide is placed. The solution is finally oxidised with 1 c.c. of 30 per cent. neutral hydrogen peroxide, and titrated.

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[1] *J. Gasbeleucht*, 1905, 48, 977; *Chem. Centr.*, 1905, II., 1831.

III. PYRITES[1] (and other Metallic Sulphides)

Pyrites is generally received in sealed duplicate samples of 200 to 300 g., the average sample being prepared according to the rules given on p. 9.

The most important estimation for the acid manufacturer is naturally the determination of the sulphur content. In addition to this, moisture, less frequently copper, arsenic, zinc, and carbonates are determined. The complete analysis of pyrites is very seldom undertaken, generally only in examining the first consignments of this raw material.

1. Moisture.—The coarsely ground sample is dried at 105°, until the weight becomes constant. For the following tests, the finely divided average sample preserved in a well-sealed bottle, not the dried sample, is employed.

The analytical results are calculated on the dry pyrites, for which reason a special moisture determination in the average sample is necessary.

2. Sulphur.—It must be decided whether the total sulphur, or that rendered soluble by aqua regia, or finally that recoverable by heating in a current of air, is to be determined. Sulphur present as heavy spar or galena would be included in the first case, which is useless for the production of sulphurous acid. For this reason and also because of its greater rapidity, and the avoidance of the fusion, which strongly attacks the platinum crucible, the wet method, as recommended by Lunge,[2] is almost universally used. By publication in the *Alkali Makers' Handbook* the method has attained the rank of a standard process, and is generally employed in buying and selling.

The third group of methods in which the available sulphur is estimated has been dealt with under "Gas Residuals" (p. 270); it is not as a rule employed for pyrites.

As a preliminary to any method of determination it is essential to reduce the sample to a very fine powder, first in a steel mortar and finally in an agate mortar. A porcelain or Wedgwood mortar should not be used, as they yield quite appreciable quantities of foreign matter to the sample. The complete sample is then sifted through very fine silk gauze, without elimination of any residue.

Lunge's method for the wet extraction of pyrites is as follows:—0·5 g. of the pyrites is treated with about 10 c.c. of a mixture of 3 volumes nitric acid of 1·4 sp. gr. and 1 volume strong hydrochloric acid (both acids must be tested for complete freedom from sulphuric acid), with occasional heating, and care being taken to avoid spurting (*cf.* p. 22).

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[1] *Cf.* G. Lunge, *Sulphuric Acid and Alkali*, 3rd edition, 1903, p. 34.

[2] *Z. anal. Chem.*, 1881, **20**, 419; and, *Z. angew. Chem.*, 1889, **2**, 473.

In exceptional cases some free sulphur may separate; if so, it may be oxidised by the cautious addition of potassium chlorate. The mixture is evaporated to dryness on the water-bath and this evaporation is repeated after the addition of 5 c.c. of hydrochloric acid, after which nitrous fumes should cease to be evolved. A further 1 c.c. of concentrated hydrochloric acid is added to the residue on the water-bath, and after a few minutes 100 c.c. of hot water are added, the whole filtered through a small filter paper and the insoluble matter washed with hot water.[1] The residue may be dried, ignited, and weighed. It may contain in addition to silica and silicates, barium, lead, and occasionally calcium sulphate, the sulphuric acid of which being absolutely non-available is purposely neglected. If the residue is not to be estimated, the filtration may be neglected and the precipitation with ammonia proceeded with as soon as all the nitric acid has been driven off.

To remove the iron, the filtrate and washings are treated with ammonia in not too large excess and heated to 60° to 70° for ten to fifteen minutes, but the solution should not be heated to boiling; it should still smell strongly of ammonia, otherwise the precipitate may contain basic ferric sulphate.

According to Treadwell,[2] the separation of basic ferric sulphate and consequent retention of sulphuric acid during washing need not be feared if the solution is supersaturated with ammonia in the cold, instead of as described above, and then heated almost to boiling with constant stirring. The separated ferric hydroxide is filtered off and washed. The operation may be carried out in shorter time (one-half to one hour) by observing the following precautions:—1. Filtering hot and washing on the filter with hot water, taking care to avoid channels by thoroughly disturbing the whole precipitate with each washing. 2. Using a sufficiently dense but rapid filtering paper. 3. Employing a correctly made funnel with an angle of 60°, the tube of which fills completely with the filtrate.

The washing is continued until about 1 c.c. of the washings yields no turbidity with barium chloride after standing several minutes. In doubtful cases it is advisable to prove the complete absence of basic sulphate by fusing the dried ferric hydroxide precipitate with pure sodium carbonate and examining the aqueous extract of the melt for sulphuric acid.

Hundreds of check tests, carried out in the manner described, have shown (Lunge) that by observing the above precautions even novices almost always obtain a ferric hydroxide free from sulphuric acid, and that with experienced workers this is always the case. Küster and

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[1] *Cf.* Dennstedt and Hassler, *Z. angew. Chem.*, 1905, **18**, 1137 and 1562; also, G. Lunge, *ibid.*, 1905, **18**, 1656.

[2] *Analytical Chemistry*, vol. ii., p. 282.

Thiel,[1] who incorrectly assume that the ferric hydroxide cannot be completely freed from sulphuric acid by washing, recommend as an alternative method to precipitate with barium chloride without previous removal of the ferric hydroxide but to subsequently remove this by prolonged digestion with hydrochloric acid, or to add a considerable amount of ammonium oxalate so as to altogether prevent the precipitation of the iron. Both methods occupy much more time than that described above and are in no way more exact.[2]

The combined filtrate and washings should not exceed 300 c.c.; if they do they must be concentrated by evaporation. The solution is acidified with pure hydrochloric acid, avoiding any considerable excess, heated to distinct boiling, and after removal of the flame a solution of barium chloride, also at the boiling temperature, added all at once with constant stirring. By adding the hot barium chloride solution all at once to the solution to be precipitated, instead of drop by drop, an error is introduced owing to the absorption of some barium chloride by the barium sulphate, but this just compensates the loss caused by the solubility of the barium sulphate in the solution, and the error due to the unavoidable co-precipitation of double sulphates of barium and ammonium. The presence of copper introduces no error in the determination; zinc if present in small quantities has also no effect, but if present in larger proportions, as in the analysis of blende, the error is greater, owing to the solubility of barium sulphate in the ammonium salts necessary to keep the zinc in solution. This error is, however, also compensated, as stated above, by adding the barium chloride solution all at once.[3] Twenty c.c. of a 10 per cent. barium chloride solution diluted with 100 c.c. of water, will suffice for $\frac{1}{2}$ g. of pyrites. A larger excess of barium chloride is to be avoided, or the results will come out too high. The whole is allowed to stand for forty minutes after precipitating, by which time the filtrate should have cleared completely and be ready for further treatment without the necessity of first waiting several hours, as in the method previously described. The clear liquid is decanted as completely as possible through a filter, 100 c.c. of boiling water poured on to the precipitate and the whole stirred; after two to three minutes the solution should have cleared again and be ready for a further decantation. The washing by decantation is repeated three or four times until the liquid ceases to show an acid reaction; the precipitate is then washed on the filter, dried and ignited. It should be perfectly white and should not cake. The filter paper, after separating the precipitate, is either burnt in a platinum spiral, or

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[1] *Z. anorg. Chem.*, 1899, **19**, 97; 1900, **22**, 424.

[2] *Cf.* Lunge, *Z. anorg. Chem.*, 1899, **19**, 454; Herting, *Z. angew. Chem.*, 1899, **12**, 274; also, *Chem. Zeit.*, 1899, **23**, 768.

[3] Lunge and Stierlin, *Z. angew. Chem.*, 1905, **18**, 1921.

the filter paper and precipitate are burnt wet in the crucible. In the latter case it is necessary to convert the resulting barium sulphide into sulphate, by gentle ignition with the crucible in a slanting position. One part $BaSO_4$ is = 0·1373 parts of sulphur.

With practice, the total volume of solution to be precipitated with barium chloride will not exceed 300 c.c., so that evaporation, before precipitating, should not be necessary. If it is unavoidable it must be carried out on the water-bath, or in such manner that any sulphurous combustion products are kept away from the solution, *e.g.* by heating on an asbestos or aluminium plate.

Other methods for removing the iron are described by Heidenreich[1] by Herting and Lehnhardt,[2] and by Gyzander.[3]

The previous precipitation of the iron is necessary, since, if present, it gives rise to the formation of a double sulphate of iron and barium in the barium precipitate, which double sulphate loses part of its sulphuric acid on ignition.[4] The resulting error may, according to Lunge, reach a maximum of $\frac{1}{2}$ per cent. in the case of pyrites (this result differing from that of Thiel, who lost up to 7 per cent.); it is, however, avoided by precipitating the iron as described on p. 273.

The injurious effect of a large excess of barium chloride, owing to absorption by the barium sulphate precipitate, has long been known, and Lunge has drawn special attention to this point. Richards and Parker[5] have carefully investigated the subject, but the methods of purification suggested by them, in addition to being extremely troublesome, fail in their purpose unless the solubility of barium sulphate in the solution for precipitation be taken into account. Richards states that under ordinary conditions the two errors exactly compensate each other, and a result very near the truth may consequently be expected if the details given above are carefully followed.

Such methods as solution of the pyrites in fuming nitric acid, or in hydrochloric acid and potassium chlorate or sodium chlorate,[6] or in hydrochloric acid saturated with bromine, are less satisfactory than that described above, owing to the liability to separation of sulphur.

Of the dry methods of analysis, that of Fresenius,[7] though somewhat tedious, is probably the most exact. 0·5 g. of pyrites is fused with 10 g. of a mixture composed of two parts of sodium carbonate and one part of potassium nitrate, the melt is extracted with water, and after precipitation of the lead by a slow current of carbonic anhydride, the

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[1] *Z. anorg. Chem.*, 1899, **20**, 233.

[2] *Chem. Zeit.*, 1899, **23**, 768.

[3] *Chem. News*, 1906, **93**, 213.

[4] *Cf.* Jannasch and Richards, *J. prakt. Chem.* 1889, **39**, 321 ; also, correction by these authors in consequence of communication from Lunge, *ibid.*, 1889, **40**, 236. See also Lunge, *Z. angew. Chem.*, 1889, **12**, 473.

[5] *Z. anorg. Chem.*, 1895, 8, 413.

[6] Noaillon, *Z. angew. Chem.*, 1897, **10**, 351.

[7] *Z. anal. Chem.*, 1877, **16**, 335.

solution is boiled with sodium carbonate solution, filtered, and washed with hot water. The combined filtrate and washings are acidified with hydrochloric acid, evaporated several times with additions of hydrochloric acid to remove the nitric acid, the residue taken up with dilute hydrochloric acid and precipitated by barium chloride, the barium sulphate precipitate after ignition being finally purified by boiling with hydrochloric acid. This is a lengthy process, and has been replaced by Lunge's method even in Fresenius' laboratory.

Other dry methods are generally restricted to the determination of sulphur in burnt ore (see p. 294), to a preliminary testing of iron pyrites, or to the analysis of some special pyrites for which the wet method is less suitable. The wet method is always the best for pyrites, which, like the Spanish, contain only about 4 per cent. of copper. The method used in Freiberg is to heat 1 g. of powdered pyrites to a red heat in a muffle furnace with 2 g. of sodium carbonate and 2 g. of potassium nitrate; the melt is extracted with hot water, filtered into excess of hydrochloric acid, and titrated with barium chloride solution by Wildenstein's method (cf. *infra*). According to M. Liebig,[1] twenty to twenty-four such tests can easily be performed in six to eight hours. Böckmann heats 0·5 g. pyrites with 25 g. of a mixture of six parts sodium carbonate and one part potassium chlorate gradually until fusion has occurred and oxygen ceases to be evolved, then extracts and precipitates with barium chloride (*cf.* p. 295). According to Treadwell, this method gives the same results as that of Fresenius; its use is practically confined to the estimation of the sulphur content of pyrites cinders (*cf.* p. 294).

The best dry methods of treatment appear to be those in which sodium peroxide is employed, as, for example, those recommended by Hempel and by Höhnel and Glaser.[2] List[3] recommends the following simplification of a method proposed by Fournier:—0·5 g. of the finely divided pyrites (or burnt ore) is intimately mixed with 5 to 6 g. of powdered sodium peroxide in a wrought-iron crucible, which is then covered and gently heated in a Bunsen flame. Reaction quickly sets in and is complete in one minute. As soon as the mass is fused the flame is removed and the crucible plunged into 150 to 200 c.c. of warm water, in which the melt quickly dissolves. The contents of the crucible are washed out and the solution approximately neutralised with 10 c.c. concentrated hydrochloric acid, filtered from the insoluble ferric hydroxide, which is washed as recommended on p. 273, and the barium sulphate precipitated as there described. List states that in absence of sulphate of lead or of alkaline earth metals, the results agree with those obtained by Lunge's wet method. The iron crucibles are cheap and will stand fifty fusions.

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[1] Post, *Chemisch.-technische Analyse*, 2nd edition, vol. i., p. 677.

[2] *Chem. Zeit.*, 1894, 18, 1448.

[3] *Z. angew. Chem.*, 1903, 16, 414.

Clark[1] heats with sodium bicarbonate and magnesia, and estimates the resulting sulphuric acid gravimetrically. Fahlberg and Iles[2] fuse with a large excess of potassium hydroxide in a silver crucible.

Of methods intended for the estimation of *available sulphur*, that is, of such sulphur as is converted into sulphur dioxide on roasting, that of Zulkowsky has been described under Gas Residuals (p. 270). Similar methods have been previously described by Mixter,[3] Brügelmann,[4] and Sauer;[5] more recently by Jannasch.[6] These methods have not been adopted in general practice for the examination of iron pyrites; they are, however, useful in the case of mixed pyrites and the like.

Other methods depend on the reduction of the FeS_2 to FeS, which is then decomposed by hydrochloric acid, the sulphuretted hydrogen so evolved being passed into iodine solution and estimated by titrating back the excess of the latter. Such methods have been described by Gräger,[7] Treadwell,[8] and Eliasberg,[9] but none have found much acceptance in practice.

The sulphuric acid formed in all the foregoing instances is estimated, in all exact work, by precipitation with barium chloride, as described on p. 274.

Silberberger[10] has proposed to replace barium chloride in the gravimetric method by precipitating the sulphuric acid in alcoholic solution with strontium chloride. This suggestion has been opposed by Lunge,[11] and the method has been rejected by the Analysis Committee of the International Congress of Applied Chemistry.[12]

Numerous proposals have been made to shorten the determination of fixed sulphuric acid by employing a volumetric method. Such methods, however, in spite of the contrary view of Teschmacher and Smith,[13] do not possess the exactness of the gravimetric determination, and further, the saving of time, unless many determinations are made simultaneously, is not considerable. At the same time it is to be borne in mind that the gravimetric determination of sulphuric acid as barium sulphate is by no means one of the most exact analytical operations, and may, in spite of all precautions, give an error amounting to $\frac{1}{200}$ of the whole, or many times that involved in the estimation of chlorine as silver chloride.

The more important volumetric methods for the estimation of fixed sulphuric acid are appended, although, as stated, they are not sufficiently accurate to justify their use in the case of pyrites.

[1] *J. Soc. Chem. Ind.*, 1885, **4**, 329 and 724.

[2] *Ber.*, 1878, **11**, 1187.

[3] *Amer. Chem. J.*, 1880-81, **2**, 396.

[4] *Z. anal. Chem.*, 1873, **12**, 32.

[5] *Ibid.*, 1876, **15**, 175.

[6] *J. prakt. Chem.*, 1889, **40**, 239; 1890, **41**, 566.

[7] *Dingl. polyt. J.*, 1883, **248**, 53.

[8] *Ber.*, 1891, **24**, 1937; 1892, **25**, 2377.

[9] *Z. anal. Chem.*, 1889, **28**, 240.

[10] *Ber.*, 1903, **36**, 2755, 4259.

[11] *Ber.*, 1903, **36**, 3387. *Z. angew. Chem.*, 1904, **17**, 913, 949; 1905, **18**, 449.

[12] *Report*, 1906, p. 344.

[13] *Chem. News*, 1871, **24**, 61, 66, and 140.

Wildenstein[1] titrates with a normal solution of barium chloride, and determines the end-point by testing a small filtered sample as follows:—The solution is placed in an inverted bell-jar A (Fig. 121), through the neck of which passes a bent tube *b*, which is closed below by a spring clip *z* and ends above in a funnel *f* bent downwards, which is closed with two thicknesses of filter paper covered and held in position with muslin. The level of acidified solution must extend above the funnel. The barium chloride solution is run into this with good stirring, and after each addition a filtered sample is withdrawn by first allowing several c.c. to flow through *f* and pouring them back into A, and then drawing a further sample and testing this with a drop of barium chloride solution. If a precipitate results, the sample is poured back into A, more barium chloride added, and a further test made. Should the end-point be overstepped, a few c.c. of normal sulphuric acid are added to the solution and the testing completed, the volume of acid added being subtracted from the volume of barium chloride used

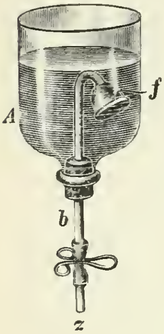

FIG. 121.

Wilsing[2] exactly neutralises the sulphate solution, using phenolphthalein as indicator, heats to boiling in a porcelain dish, and adds a measured quantity of a 4 per cent. barium chloride solution together with phenolphthalein, and then titrates with a 2 per cent. solution of sodium carbonate until the red coloration is obtained. The volume of carbonate solution required gives the excess of barium chloride added.

Similar methods have been described by Carl Mohr,[3] Knöpfler,[4] Monhaupt,[5] Blacher and Koerber,[6] and others.

Andrews[7] precipitates the sulphuric acid by adding excess of a hydrochloric acid solution of barium chromate to the boiling solution of the sulphate; the excess of the precipitating reagent is removed by addition of ammonia or of calcium carbonate to the boiling solution, the whole filtered, and washed with hot water. The filtrate, which contains alkali chromate corresponding to the sulphate originally present, is cooled, concentrated hydrochloric acid added, followed by potassium iodide, and the liberated iodine titrated with sodium thiosulphate. According to Reuter,[8] only 5 c.c. of concentrated hydrochloric acid should be added, the whole washed for five minutes after the addition of the potassium iodide, the beaker being kept covered and a current of carbon dioxide passed over the surface of the solution.

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[1] *Z. anal. Chem.*, 1862, 1, 432.

[2] *Chem. Ind.*, 1886, **9**, 25.

[3] *Cf.* Mohr-Classen, *Lehrbuch der Chem. analyt. Titrirmethoden*, 7th edition. 1896, pp. 150-154.

[4] *Annalen*, 1885, **230**, 260.

[5] *Chem. Centr.*, 1905, **I.**, 296.

[6] *Ibid.*, 1905, **II.**, 511.

[7] *Chem. Zeit. Rep.*, 1889, **13**, 39.

[8] *Chem. Zeit.*, 1898, **22**, 357.

(The analytical results given in the paper do not show any very high degree of accuracy.)

Marboutin and Moulinié[1] describe a similar method in which equivalent solutions of barium chloride and of potassium chromate are employed. The sulphuric acid is precipitated in acid solution by barium chloride, and the excess of this reagent precipitated by addition of potassium chromate; the excess of the latter is then determined by iodine or by arsenious acid. An almost identical method is recommended by Telle.[2] He employs (1) a solution containing 12·07 g. $BaCl_2 2H_2(2H_2O)O$ per litre (=4 g. SO_3); (2) a solution of potassium bichromate equivalent to this, and containing 7·3635 g. per litre; (3) a solution containing 38 g. sodium thiosulphate per litre; and (4) a 10 per cent. solution of potassium iodide. The thiosulphate equivalent of the bichromate solution is obtained by treating 10 c.c. of solution No. 2 with 5 c.c. of solution No. 4, and titrating the liberated iodine with solution No. 3 after addition of distilled water and excess of hydrochloric acid. One molecule of potassium bichromate (294·54) liberates six molecules of iodine, and thus corresponds to 6×248·3 of thiosulphate, or 2×244·37 of $BaCl_2, 2H_2O$, according to the equation:—

$$2BaCl_2 + K_2Cr_2O_7 + 2NH_3 + H_2O = 2BaCrO_4 + 2KCl + 2NH_4Cl.$$

Grossmann[3] decomposes the neutral solution of the sulphate with barium hydroxide, filters off one-half, precipitates the excess of baryta with carbon dioxide, boils, cools, dilutes to 500 c.c., and titrates one-half of the clear solution with normal acid. Employing the $\frac{1}{20}$ equivalent of sodium sulphate = 3·554 g., the percentage content in Na_2SO_4 is equal to eight times the number of c.c. of normal hydrochloric acid required; a correction of 0·4 per cent. must be made for the volume occupied by the barium precipitate. Finally, there also remains a constant loss of 1·3 per cent., the cause of which has not been determined, but which must nevertheless be allowed for; this renders the process useless for exact determinations.

Nikaido[4] precipitates the sulphate in alcoholic solution by addition of $N/10$ lead nitrate solution, using potassium iodide as indicator. The method is only applicable in special cases.

Riegler[5] precipitates the sulphate with a known quantity of barium chloride, treats with iodic acid, filters off the barium iodate, and arrives at the quantity of barium used by measuring, in the nitrometer, the nitrogen evolved on addition of hydrazine sulphate.

Recently, methods first proposed by Vaubel,[6] and based on the use

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[1] *Chem. Centr.*, 1898, **I.**, 218.

[2] *Ibid.*, 793.

[3] *Chem. News*, 1880, **41**, 114; *Ber.*, 1880, **13**, 824.

[4] *J. Amer. Chem. Soc.*, 1902, **24**, 774.

[5] *Z. anal. Chem.*, 1902, **41**, 17.

[6] *Ibid.*, 1896, **35**, 821.

of benzidine, have attracted attention. W. A. Müller[1] has found that fixed sulphuric acid can be quantitatively precipitated by benzidine hydrochloride when the latter is present in sufficient excess, and that such excess can be directly determined by titration with alkali. This is due to benzidine being such a very weak base, that the hydrochloride is sufficiently dissociated hydrolytically in solution to behave like free hydrochloric acid towards phenolphthalein. The decomposition corresponds to the equation :—

$$R_2SO_4 + C_{12}H_{12}N_2.2HCl = 2RCl + C_{12}H_{12}N_2.H_2SO_4.$$

The solution of benzidine hydrochloride employed contains about 30 g. per litre, and is standardised against barium or sodium hydroxide by means of normal acid, using phenolphthalein as indicator. (This indicator should be avoided. *Cf.* p. 97.) The decomposition must be carried out in warm solution, since in the cold the separated sulphate carries down some of the hydrochloride. The heating is done in a 250 c.c. flask on the water-bath, and the solution maintained hot for some minutes; in the presence of volatile acids the flask should be stoppered. The solution is rapidly cooled and made up to a definite volume, filtered through a dry filter paper, and the excess of hydrochloride determined by titrating an aliquot portion with standard alkali and phenolphthalein.[2]

Raschig[3] has modified this method as follows. Forty g. of benzidine are ground up with 40 c.c. of water, washed with about 750 c.c. of water into a litre flask, 50 c.c. of concentrated hydrochloric acid added, and then water to the graduation mark. On shaking, the whole or the greater part dissolves to a brown solution, which is filtered if necessary, and then diluted to twenty times its volume. One hundred and fifty c.c. of this weak solution are used to precipitate 0·1 g. sulphuric acid. The sulphate solution to be examined is allowed to flow, with continual stirring, into the benzidine solution, and the benzidine sulphate which rapidly separates is filtered off at the pump. A 200 c.c. funnel, fitted with a Witt's filter plate, is used for the filtration. The plate, which is of 40 mm. upper diameter, is covered by two moistened filter papers of 46 mm. diameter, the extending edges of which are, after applying the suction, pressed by means of a sharp-angled glass rod to form a circular pad, and so make the filter perfectly tight. Any precipitate adhering to the walls of the beaker or other vessel used for the precipitation is washed off with a portion of the clear filtrate, and as the last drop of mother liquor drains off from the filter, the precipitate is washed twice successively with from 5 to 10 c.c. of water.

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[1] *Ber.*, 1902, **35**, 1587.

[2] *Cf.* also, Müller and Dürkes, *Z. anal. Chem.*, 1903, **42**, 477; Müller, *Z. angew. Chem.*, 1903, **16**, 1017.

[3] *Z. angew. Chem.*, 1903, **16**, 617 and 818.

By thus washing with a minimum quantity of water, the objection raised by W. A. Müller and others to the method on the grounds of the solubility of benzidine sulphate in the wash-water, is overcome. The funnel is removed from the filter-flask, placed on a watch-glass of 50 to 60 mm. diameter, inverted, the filter-plate and precipitate transferred to the watch-glass by the aid of a glass rod, the filter-plate removed, the filter pressed together in the fingers and dropped into an Erlenmeyer flask of 250 c.c. capacity and 30 mm. wide at the neck. The watch-glass and funnel are washed with not more than 25 c.c. of water, and the washings added to the contents of the flask, which is then closed with a rubber stopper and well shaken until there results a uniform magma of precipitate and disintegrated filter paper quite free from small lumps of benzidine sulphate. The mixture is then warmed to 50°, and after addition of phenolphthalein titrated with *N*/10 sodium hydroxide solution, finally heating to boiling to remove from the solution all carbon dioxide, since it affects the indicator. An accidental excess of alkali solution may be titrated back with normal acid. This method is applicable to the estimation of sulphuric acid present either in the free state or as copper or ferrous sulphate; it is not directly applicable to ferric sulphate, as in this case the iron must be precipitated as described on p. 273. The method is also inapplicable in many other cases, as for example in the presence of certain organic compounds.

The benzidine method may, moreover, be used even in the presence of iron when not more than 1 atom of sulphur is present per 1 atom of iron, provided that (as first recommended by M. Schlötter) ferric salts are first reduced to the ferrous state. For this purpose, Raschig[1] employs a dilute solution of hydroxylamine hydrochloride, and gives the following details for the determination of sulphur in pyrites by this method. Exactly 0·8 g. of the finely divided sample is weighed into a 200 c.c. conical flask, 5 c.c. of fuming nitric acid added, and the flask with a small funnel in the neck heated on the water-bath. After half an hour, 30 c.c. of water are added, the whole of the contents rinsed into a 100 c.c. flask, made up to the mark and well shaken. Twenty c.c. of this solution are then placed in a 600 c.c. beaker, 10 c.c. of a 1 per cent. solution of hydroxylamine hydrochloride added, and 500 c.c. of benzidine hydrochloride solution prepared as above. The precipitation and subsequent treatment of the benzidine sulphate is then carried out as described. The filtrate from the sulphate should always be tested with barium chloride, to make sure that sufficient benzidine solution has been used for complete precipitation.

3. **Arsenic.**—The estimation of arsenic in pyrites is somewhat laborious, and is consequently not carried out in works as frequently as

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[1] *Z. angew. Chem.*, 1905, **18**, 331; 1906, **19**, 331.

its importance would demand. The arsenic in pyrites not only finds its way into the vitriol, but also into the hydrochloric acid prepared therefrom, and may, in this and in many other cases, prove very harmful. The methods employed for its determination lead, unfortunately, to widely differing results.

According to the method devised by Reich, as modified by M'Cay,[1] 0·5 g. pyrites is treated with strong nitric acid in a porcelain crucible, the free acid evaporated without taking the mixture to dryness, 4 g. of sodium carbonate added, and the whole taken to dryness on the sand-bath, after which 4 g. of potassium nitrate are added, and the mixture heated to gentle fusion for ten minutes. The melt is extracted with hot water, filtered, and the filtrate, after acidifying with a little nitric acid, heated for some time to remove all carbon dioxide, and after addition of silver nitrate, cautiously neutralised with dilute ammonia. The precipitate, which contains all the arsenic as silver arsenate, is dissolved in dilute nitric acid, and the silver either estimated by titration with ammonium thiocyanate according to Volhard's method, or the solution evaporated in a platinum dish and the residue weighed. One part $Ag_3AsO_4 = 0·1621 As$. If it be desired to precipitate the arsenic as arsenic pentasulphide, the solution is transferred to a flask, acidified with hydrochloric acid, the flask almost filled with air-free water and saturated with sulphuretted hydrogen. The stopper is then securely fastened and the flask heated for an hour on the water-bath, whereby a precipitate of the pentasulphide, uncontaminated with free sulphur, is obtained.

Other methods give results which differ rather widely from those obtained as above.

Blattner and Brasseur[2] quote an instance in which different analysts found from 0·19 to 0·57 per cent. of arsenic, and another in which the figures varied from 0·05 to 0·39 per cent. Records of still greater differences may be found in the journals. They recommend the following process:—

1. *Wet treatment.* Ten g. of pyrites is added gradually with gentle warming to aqua regia, prepared from 125 c.c. nitric acid of sp. gr. 1·37, 250 c.c. hydrochloric acid of sp. gr. 1·15 to 1·17, and 100 c.c. water, in a litre flask. The bulk of the nitric acid is driven off by evaporation after addition of hydrochloric acid; since all the arsenic is present as arsenic acid, no loss through evolution of arsenious chloride is said to take place. After the addition of 100 c.c. of water, the solution is cooled and filtered, ammonia is added until a slight precipitate of ferric hydroxide is formed, sulphurous anhydride passed through the cold solution until the reduction of the iron to the ferrous state is complete,

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[1] *Chem. News*, 1883, **48**, 7. *Amer. Chem. J.*, 1886, **8**, 77; 1887, **9**, 174; 1888, **10**, 459.

[2] *Bull. Soc. Chim.*, 1897 [3], **17**, 13.

the excess of sulphur dioxide removed by warming, and after cooling to 60°-70°, the arsenic precipitated by passing in sulphuretted hydrogen for six to seven hours. The solution is then allowed to stand for twelve hours, and filtered. The precipitate is washed with water containing hydrochloric acid and sulphuretted hydrogen until all the iron has been removed, and finally with distilled water.

It is then dissolved by digesting the precipitate and filter paper with ammonium carbonate, and the solution filtered. The filtrate is rendered strongly acid with hydrochloric acid warmed to 50°-70°, and the arsenic precipitated as arsenious sulphide by passing in sulphuretted hydrogen for an hour. The arsenic in the precipitate may be determined either as magnesium ammonium arsenate or as silver arsenate. In the former case the precipitate is dissolved in strong ammonia, evaporated to dryness on the water-bath, taken up with 10 c.c. nitric acid, and after a further slight evaporation, rendered ammoniacal, and a small quantity of alcohol, followed by magnesia mixture, added; after standing for twelve hours, the precipitate is collected on an ash-free filter paper, washed with a solution of one part of ammonium chloride and one of alcohol in three of water, dried, and ignited after separation from the filter paper. The filter paper is ignited separately after addition of a small quantity of ammonium nitrate. One hundred parts $Mg_2As_2O_7$ correspond to 48·28 parts As.

2. *Dry treatment.* Two g. of pyrites are thoroughly mixed in a platinum crucible of 30 c.c. capacity with 10 to 12 g. of a mixture of equal parts of potassium nitrate and sodium carbonate, and covered with a layer of 2 g. of the same mixture. The crucible is then covered and heated over a Bunsen flame 3 cm. high. When the reaction is complete, the mass is allowed to cool, the contents of the crucible placed in 70 c.c. of boiling water, and after solution, the whole filtered and the residue washed with boiling water. All the arsenic is then in the filtrate as arsenate. The solution is acidified with nitric acid, heated to boiling, allowed to cool, rendered exactly neutral by ammonia, and after the addition of one drop of nitric acid, again neutralised until a drop of the solution only produces a blue tint on red litmus paper after some seconds. Silver nitrate is then added, drop by drop, until no further precipitation occurs; the silver arsenate is collected on a filter and washed with cold water until the filtrate no longer gives a turbidity with hydrochloric acid. The silver arsenate is dissolved on the filter in very dilute nitric acid, 5 c.c. of a sulphuric acid—nitric acid—iron solution added as indicator, and the solution titrated with *N*/10 ammonium thiocyanate solution to the appearance of a rose coloration. Each 1 c.c. of the thiocyanate solution corresponds to 0·0025 g. As. This method is rapid, and the results obtained agree very closely with those obtained by the first method, and also with

those of Clark, who employs a mixture of magnesia and sodium hydroxide for fusing the ore (cf. *infra*).

This second method of Blattner and Brasseur is to be preferred to the first, since a loss of arsenic by volatilisation as arsenious chloride may occur in the latter.

The same authors have also described a method[1] based on the precipitation of the arsenic as tri-iodide and the subsequent volumetric estimation of the latter.

List[2] heats 2 g. pyrites with 10 g. sodium peroxide in a crucible, as described on p. 276. By this treatment all the arsenic is converted to arsenic acid, which may be estimated as in the method of Blattner and Brasseur.

Clark[3] has devised the two following methods for the estimation of arsenic in pyrites:—

1. *Precipitation method.* About 3 g. of the ground sample is mixed with four times its weight of a mixture of equal parts of freshly calcined magnesia and pure sodium hydroxide previously ground together in a porcelain mortar, and the whole heated for about ten minutes in an uncovered platinum crucible; the mixture contracts slightly, but does not fuse. The product is extracted with hot water, and the filtrate acidified with hydrochloric acid, whereby sulphuretted hydrogen is freely evolved. On boiling the nearly colourless solution thus obtained for a few minutes, the arsenic separates as sulphide. After saturation with sulphuretted hydrogen to ensure complete precipitation, the precipitate is filtered off, washed, the arsenic trisulphide dissolved in ammonia, and the resulting solution evaporated to dryness on the water bath. The residue is dissolved in a small quantity of strong nitric acid and the arsenic estimated as magnesium ammonium arsenate, or precipitated as silver arsenate, and its weight calculated from the silver found, as determined by titration by Volhard's method, or by cupellation according to Richter.

The method gives very accurate results, and is applicable even when the arsenic is only present in very small quantity.

2. *Distillation method.* About 1·7 g. of the finely powdered pyrites mixed with six times its weight of the magnesia-sodium hydroxide mixture is heated over a Bunsen flame of medium height in an uncovered platinum crucible for one hour, by which time oxidation should be complete. The contents of the crucible are transferred to a flask, moistened with water, and dissolved in about 70 c.c. of strong hydrochloric acid. It is necessary to heat towards the end, until all action ceases. The flask is fitted with a funnel tube which dips below the surface of the liquid, and it is further connected with a

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[1] *Z. angew. Chem.*, 1904, **17**, 1727.

[2] *Ibid.*, 1903, **16**, 415.

[3] *J. Soc. Chem. Ind.*, 1887, **6**, 352.

small glass cooling-worm, to the end of which a straight calcium chloride tube is attached. A considerable excess of reducing agent, dissolved in strong hydrochloric acid, is then admitted through the funnel tube. The reducing agent employed is cuprous chloride, which forms a readily soluble double salt with sodium chloride, and reduces quite as readily as a ferrous salt. A mixture of cuprous and ferrous chlorides, obtained by dissolving copper in ferric chloride, also forms an excellent reducing agent. The contents of the flask are then slowly distilled into water for an hour, after which about 30 g. of strong hydrochloric acid are added and the distillation continued for a further half-hour. All the arsenic should now be in the receiver, but it is advisable to check this by adding more hydrochloric acid, changing the receiver, and testing the fresh distillate collected. The arsenic so recovered may be precipitated as sulphide and collected on a tared filter paper, or it may be titrated with iodine in the usual manner.

The distillation method requires less time than any other, and gives equally exact results even for small amounts of arsenic. It may also be employed with advantage in estimating the arsenic in metallic copper.

According to H. Fresenius,[1] the fusion method offers no advantages over that of direct distillation in the presence of ferrous chloride, where the solution has been treated hot with chlorine or with hydrochloric acid and potassium chlorate.

The method of determining arsenic proposed by Kühn and Säger,[2] which consists in obtaining and weighing an arsenic mirror, is too troublesome for technical work.

The methods for detecting and estimating traces of arsenic are described on pp. 362 to 376.

4. **Copper.**—The following process is employed at the Duisburg copper works, and was first described in the *Alkali Makers' Handbook*. Five g. of the pyrites, ground and dried at 100°, are gradually dissolved in 60 c.c. nitric acid of sp. gr. 1·2 in an inclined Erlenmeyer flask. As soon as the violence of the reaction is over, the flask is warmed and evaporation allowed to proceed until sulphuric acid vapours are given off. The dry residue is dissolved in 50 c.c. hydrochloric acid of sp. gr. 1·19, and after the addition of sodium hypophosphite (2 g. sodium hypophosphite, NaH_2PO_2, dissolved in 5 c.c water) the solution is boiled for a time to remove arsenic and to reduce the ferric chloride. An excess of strong hydrochloric acid is then added, the solution diluted with about 300 c.c. of hot water, sulphuretted hydrogen passed in, and the precipitate filtered off and thoroughly washed. A hole is made in the filter by means of a glass rod, the precipitate washed back into the precipitating flask, and the metallic sulphides adhering to the filter

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[1] *Z. anal. Chem.*, 1888, **27**, 34; *cf.* also, Nahnsen, *Chem. Zeit.*, 1887, **11**, 692.

[2] *Ber.*, 1890, **23**, 1798.

paper as well as the main bulk of precipitate, brought into solution by treatment with nitric acid; the solution in the flask is then evaporated to dryness on the water-bath, and the residue again taken up with nitric acid and water, neutralised with ammonia and dilute sulphuric acid added in slight excess. When cold, the solution is filtered to remove lead sulphate and other insoluble matter, the flask and the filter being washed with water containing sulphuric acid, 3 to 8 c.c. of nitric acid of sp. gr. 1·4 added to the filtrate, and the copper deposited electrolytically. From the weight of copper found, 0·01 per cent. is deducted for the simultaneously deposited bismuth and antimony.

Nahnsen[1] estimates the copper in pyrites as follows. The pyrites is very finely ground, dried, and 12·5 g. of the dried material are covered with 10 c.c. of water and 1 c.c. of strong sulphuric acid in a thin-walled beaker about 17 cm. deep. The beaker is covered with a porcelain dish and nitric acid of sp. gr. 1·4 added in successive small portions until frothing ceases to occur. The solution is then boiled over a fairly large flame; after several minutes the porcelain dish, which is sufficiently washed by the acid which condenses underneath, is removed and the gradually thickening solution is allowed to boil vigorously with constant agitation, until the liquid almost adheres to the glass and yellow particles of salt begin to separate. The magma is then quickly brought into solution by the addition of warm water. With some practice the whole operation may be performed in from ten to fifteen minutes. The cold solution is transferred to a 250 c.c. flask, made up to the mark and filtered through a dry filter paper. Two hundred c.c. (= 10 g. pyrites) of the solution, which is now free from silica and lead, are treated for some hours with a good current of sulphuretted hydrogen, until the precipitate becomes flocculent and the solution appears clear. The solution is then filtered and the precipitate continually pressed out by means of a glass rod and washed on the filter paper with water. It is unnecessary to wash copper sulphide with sulphuretted hydrogen water when, as in this case, the sulphuretted hydrogen has been allowed to act until the precipitate settles well and leaves a clear supernatant liquid. The portion of the precipitate remaining on the filter is washed back into the main bulk with the least possible quantity of hot water, and concentrated sodium sulphide solution added in such quantity that no sulphur remains undissolved after the solution has been brought to, and maintained for several minutes at, boiling point. After diluting with water and allowing to settle in a warm place, the solution, which contains the arsenic and antimony, which is now quite free from copper, is filtered, and the sulphide of copper washed with hot water. Traces of iron sulphide, which always adhere to the sulphide of copper (in two cases this amounted to 0·02

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[1] *Chem. Zeit.*, 1887, 11, 692.

per cent. on the pyrites), are extracted by washing with hot water acidified with a few drops of hydrochloric acid; the precipitate is then washed until free from chlorine, and the copper estimated as cuprous sulphide.

Cadmium and bismuth sulphides, present in the cuprous sulphide, are determined by dissolving the precipitate in nitric acid, and treating the warm solution for some time with ammonium carbonate. The resulting precipitate is weighed as oxide and allowed for.

Should 25 g. be taken for analysis instead of 12·5 g., the method, according to the author, is but slightly more troublesome and longer. When the pyrites contains 3 to 5 per cent. of copper, 5 g. of the sample will suffice.

A very complete account of the estimation of copper in pyrites, and more particularly of the "Cornish assay," has been published by Westmoreland.[1]

List[2] burns the pyrites in a porcelain crucible of special shape, extracts with hydrochloric acid, neutralises with ammonia, adds sulphurous acid, and precipitates the copper as cuprous thiocyanate; this is oxidised with a mixture of sulphuric and nitric acids to sulphate, and the copper determined by electrolysis.

5. **Lead.**—Lead remains in the residue in the form of sulphate when the pyrites is treated with aqua regia, as described on p. 272. The lead sulphate is extracted from the insoluble residue by warming with a concentrated solution of ammonium acetate; the resulting solution is evaporated with addition of a little pure sulphuric acid, and the residue finally dried and ignited in a porcelain dish or crucible. One part $PbSO_4 = 0{\cdot}6829$ Pb.

6. **Zinc.**—The zinc in pyrites is occasionally determined, according to Hassreidter and Prost, since it is scarcely possible to recover the sulphur combined with the zinc. Schaffner's method, as described under Zinc Blende on p. 289, is not available, owing to the large preponderance of iron, and on this latter account a gravimetric method must be resorted to. One g. of the pyrites is dissolved in aqua regia, as described on p. 272, the excess of nitric acid evaporated off, and the residue taken up with 5 c.c. of strong hydrochloric acid; water is then added and the solution treated with sulphuretted hydrogen to remove any metals yielding sulphides insoluble in acid solution. Any precipitate formed is filtered off, and the filtrate freed from sulphuretted hydrogen by boiling and oxidised with aqua regia. The oxidised solution is treated, when cold, with ammonium carbonate, until the resulting precipitate only redissolves very slowly; ammonium acetate is then added, the solution boiled for a short time, and filtered. The basic ferric acetate so precipitated carries down some of the zinc, and must,

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[1] *J. Soc. Chem. Ind.*, 1886, **5**, 49 and 277.

[2] *Z. angew. Chem.*, 1903, **16**, 416.

therefore, be dissolved in hydrochloric acid, and again precipitated as described, the operation being repeated so long as zinc can be detected in the filtrate. The combined filtrates are concentrated if necessary, and the zinc precipitated in the warm solution by sulphuretted hydrogen; the whole is then allowed to stand for twenty-four hours, the clear liquor decanted, and the zinc sulphide filtered off and washed. The precipitate and filter are treated with dilute hydrochloric acid, and the resulting solution, after boiling till free from sulphuretted hydrogen, filtered, precipitated with sodium carbonate, the zinc carbonate well washed, dried, and converted by ignition to ZnO of which one part = 0·8034 Zn. For very exact determinations any silica, oxide of iron, and alumina precipitated with the zinc oxide must be estimated and allowed for; this, however, is seldom necessary.

Mayer and Lösekann[1] have worked out a method for estimating the zinc as zinc ammonium phosphate.

7. **Carbonates of the alkaline earths** are occasionally estimated, since when present they cause sulphur to be retained, owing to the formation of the corresponding sulphates. Since their quantity is always small, the carbonic acid cannot be determined accurately by loss, and consequently a direct method must be used. The carbonic acid is liberated by addition of strong acid and absorbed in soda lime, taking care to retain moisture and any acid carried forward; either the apparatus of Fresenius[2] or that of Classen[3] may be employed for the determination. Greater rapidity and accuracy can be attained by measuring the volume of evolved gas in the Lunge and Marchlewski calcimeter[4] (p. 149).

8. **Carbon.**—It is occasionally necessary to estimate the carbon present in pyrites, especially in the products sorted out from coal and known under the name of "coal brasses."[5] This is done, according to Treadwell and Koch,[6] by combustion in a porcelain boat, as in the ordinary method of organic analysis, employing a 30 cm. layer of copper oxide and 25 cm. of lead peroxide to retain the sulphur; or more conveniently and in shorter time by oxidising with a mixture of chromic and sulphuric acids. For the latter process they follow the method of Corleis,[7] passing the gas liberated in the decomposing flask through a 10 cm. layer of glowing copper oxide, followed by 10 cm. of solid chromium trioxide, and after this through two small U-tubes each containing 3 c.c. of a solution of chromium trioxide in concentrated sulphuric acid. After leaving the U-tubes the gas is passed through a

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[1] *Chem. Zeit.*, 1886, **10**, 729.

[2] *Quantitative Analysis*, vol. i., p. 449.

[3] Mohr's *Titrirmethoden*, 7th edition, p. 641.

[4] *Z. angew. Chem.*, 1891, **4**, 229.

[5] *Cf.* Lunge, *Sulphuric Acid and Alkali*, 3rd edition, 1903, p. 41.

[6] *Z. angew. Chem.*, 1903, **16**, 173.

[7] *Stahl u. Eisen*, 1894, **14**, 587; *cf.* Vol. II., "Iron."

tube filled with glass beads moistened with sulphuric acid, then through a couple of calcium chloride tubes, and is finally absorbed in two weighed tubes filled with soda-lime. The results obtained in this manner were identical with those of the combustion method (26·26 per cent. carbon).

9. It is necessary in some instances to distinguish between **Ordinary and magnetic pyrites (Pyrrhotite),** Fe_7S_8, more especially in the case of American ores. To effect this,[1] the mineral is ground till it will pass through a sieve of sixty meshes to the inch (24 per cm.), but not finer, and the powder spread on a sheet of glazed paper. The magnetic pyrites is then picked out by the aid of a magnet and freed from any ordinary pyrites adhering mechanically, by gently tapping the magnet, after which the armature is fixed to the magnet and the magnetic ore brushed off. This operation is repeated five or six times and the sulphur separately estimated in the two portions.

IV. Zinc Blende

1. **Total Sulphur.**—0·5 g. of the very finely ground sample is covered with about 20 c.c. of a mixture of three parts strong nitric acid and one part strong hydrochloric acid, or with hydrochloric acid saturated with bromine, allowed to stand covered overnight, evaporated almost to dryness, and a few c.c. of hydrochloric acid and 50 c.c. of water added; the solution is filtered hot and precipitated with barium chloride, after removal of the iron by ammonia, as described on p. 273, should this be present in any quantity.

According to Thiel,[2] the estimation of sulphuric acid in the presence of large quantities of zinc always leads to low results, owing to the formation of complex salts on precipitation with barium chloride (with equivalent quantities of zinc the results are 0·33 per cent. too low). This source of error may be avoided if, before the addition of the barium chloride, the zinc is exactly precipitated as hydroxide by addition of ammonia and the hydroxide subsequently dissolved out of the mixed precipitate with a slight excess of hydrochloric acid before filtering.

2. **Zinc.**—According to the modified Schaffner method now employed at zinc works,[3] 2·5 g. of the blende, dried at 100° and finely ground, are treated with 12 c.c. of fuming nitric acid in an Erlenmeyer flask of 200 c.c. capacity, first in the cold and then with gentle heating to disappearance of the red fumes, when 20 to 25 c.c. of strong nitric acid are added and the whole evaporated to dryness on the sand-bath. Five c.c. of hydrochloric acid and a little water are then added and the mixture warmed until as much as possible has dissolved, after which the solution is

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[1] Cone, *J. Amer. Chem. Soc.*, 1896, **18**, 404.

[2] *Z. anorg. Chem.*, 1903, **36**, 85.

[3] Communicated by V. Hassreidter and E. Prost.

diluted with 50 to 60 c.c. of water and the whole heated to 60° to 70°, until only gangue and separated sulphur remain undissolved. A moderate current of sulphuretted hydrogen is next passed into the solution and 50 to 100 c.c. of cold water added, little by little, with continuous stirring until the precipitation of lead and cadmium sulphides is complete, which may be recognised by the transparency of the bubbles as they rise through the solution. Excessive dilution and too slow a current of sulphuretted hydrogen should be avoided. The solution is filtered and the precipitate washed with 100 c.c. of sulphuretted hydrogen water, to which 5 c.c. of hydrochloric acid have been added, until a drop of the filtrate ceases to give the reaction for zinc with ammonium sulphide. The filtrate and washings, which amount in all to about 300 c.c., are boiled to remove the sulphuretted hydrogen, the complete removal of which is checked by lead acetate paper, and the ferrous iron then oxidised by addition of 5 c.c. of strong nitric acid and 10 c.c. of hydrochloric acid. After partial cooling the solution is poured into a 500 c.c. flask, 100 c.c. of ammonia of sp. gr. 0·9 to 0·91 and 10 c.c. of a cold saturated solution of commercial ammonium carbonate added, and the whole well shaken and allowed to cool.

In the meantime an ammoniacal solution zinc of known content is prepared, by dissolving in a 500 c.c. flask chemically pure zinc, approximately equal in quantity to the zinc content of the ore, in 5 c.c. of nitric acid and 20 c.c. of hydrochloric acid diluted with about 250 c.c. of water. After solution, 100 c.c. of ammonia and 10 c.c. of a saturated solution of ammonium carbonate are added, the whole shaken, and allowed to cool. In the presence of manganese, 10 c.c. of hydrogen peroxide are added before the ammonia. When quite cold, both flasks are filled with water to the graduation mark, and the solution prepared from the ore passed through a dry, pleated filter paper. For titration, 100 c.c. are pipetted from each solution into a thick-walled glass cylinder or beaker, and each portion diluted with about 200 c.c. of water. The standard solution for titration consists of a concentrated solution of commercial sodium sulphide crystals diluted with 10 to 20 times its volume of water, so that each c.c. corresponds to 0·005 to 0·010 g. of zinc. The sodium sulphide solution is allowed to flow alternately from two adjacent 50 c.c. burettes into each of the two solutions, at first in 2 or 3 c.c. at a time, and later in such smaller quantities as may appear necessary; the solutions are stirred and a drop of each solution placed simultaneously, by means of thin glass rods, on a strip of sensitive lead acetate paper. After ten to fifteen seconds have elapsed, the drops are washed off by the aid of a small wash-bottle, and the titration with the sulphide solution continued until the drops taken from each of the solutions, after an equal lapse of time, give rise to weak but distinctly perceptible brown stains of equal intensity. Should the volume of liquid withdrawn for the tests be appreciable, the operation must be repeated; in all cases the end-reactions in the two solutions must be reached at the same time and the readings made to within 0·05 c.c.

If the quantity of pure zinc taken for the standard solution be denoted by a, the number of c.c. of the sodium sulphide solution required per 100 c.c. of the standard by b, and the number of c.c. required per 100 c.c. of the solution of the ore (=0·5 g. ore) by c, then the percentage of zinc in the ore is given by the formula $\frac{40\,ac}{b}$.

In very exact determinations a quantity of ferric chloride, corresponding to the iron content of the ore, should be added to the standard solution, to compensate for the zinc carried down with the ferric hydroxide precipitate.

F. Meyer[1] treats 0·5 g. of the ore, in an ordinary flask, with 10 c.c. of aqua regia (made up of two parts of hydrochloric to one part of nitric acid), starting cold and then warming, evaporates off the excess of acid, takes up the residue with 10 c.c. of sulphuric acid (1 : 2), and evaporates, the solution, to precipitate the lead, until dense white fumes are evolved. He then allows the solution to cool, dilutes with 60 to 80 c.c. of hot water, precipitates copper, cadmium, etc., by the addition of 10 c.c. of sodium thiosulphate solution (1 : 8), boils until the solution is nearly clear, and, after filtering from gangue, lead sulphate, etc., and boiling the filtrate with 5 c.c. of nitric acid until the sulphur has collected into globules, precipitates the iron and aluminium with 30 c.c. of ammonia of sp. gr. 0·92; finally, when nearly cold, the manganese is thrown down by the addition of 20 c.c. of bromine water. After standing for some time the bromine is expelled by boiling, the solution filtered into a thick-walled beaker, the flask and filter paper partially washed, the contents of the filter dissolved in 5 c.c. of aqua regia and collected in the flask, the iron, aluminium, and manganese precipitated as before by 20 c.c. of ammonia solution and 20 c.c. of bromine water, the filtrate added to the preceding and the two made up to 500 c.c. The solution is then allowed to stand overnight and titrated with sulphide of sodium solution, of which 1 c.c. corresponds to about 0·01 g. zinc, using a burette graduated in $\frac{1}{10}$ c.c. The preparation of the standard solution and the titration are carried out as in Hassreidter and Prost's method described above.

Jensch[2] has drawn attention to the occurrence of certain siliceous zinc ores which obstinately resist the ordinary methods of treatment.

A critical review of the various volumetric methods of estimating zinc has been published by O. Brunck.[3]

Herz[4] estimates the zinc gravimetrically by precipitation with

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[1] *Z. angew. Chem.*, 1894, **7**, 391.

[2] *Ibid.*, 155.

[3] *Chem. Zeit.*, 1903, **27**, 339.

[4] *Z. anorg. Chem.*, 1901, **26**, 90.

dimethylamine, but according to Herting this method is not to be recommended.

Herting[1] is of opinion that the gravimetric determination, by precipitating as basic carbonate and weighing as oxide, is preferable to any volumetric method.

As a rule, it is necessary to separate the zinc from the other metals. The ordinary method consists in precipitating as sulphide with sulphuretted hydrogen in acetic acid solution, or by adding ammonium sulphide. In either case great difficulty is experienced in the filtration of the sulphide, which readily passes through the filter paper. This difficulty may be quite overcome if Murmann's suggestion[2] of adding a solution of mercuric chloride before precipitation be followed; the mixed precipitate of the sulphides of zinc and mercury settles in a few minutes, and yields a clear solution on filtration. On ignition, the mercuric sulphide is completely eliminated, whilst the sulphide of zinc is converted into the oxide, even in the absence of a current of oxygen. Herting strongly recommends this mode of procedure. He also confirms the observation of Flath,[3] to the effect that zinc may be completely separated from iron by a double precipitation of the latter with ammonia, especially after the addition of ammonium acetate.

3 **Lead.**—The metallic sulphides precipitated as above (2) are, if necessary, digested with a moderately concentrated sodium sulphide solution, the resulting solution diluted, filtered, and the insoluble matter washed. The residue is dissolved in dilute nitric acid, the solution filtered and evaporated with excess of sulphuric acid, to obtain the lead in the form of sulphate. One part $PbSO_4 = 0·6829$ Pb.

4. **Calcium and Magnesium** fix sulphur during calcination, and must consequently be estimated. Two to 5 g. of the blende are digested by warming with 50 c.c. of dilute hydrochloric acid (1 : 10), the solution decanted, and the operation repeated once or twice. The residue is washed, the filtrate freed from sulphuretted hydrogen by boiling, oxidised by bromine water, and precipitated with ammonia free from carbonate. The calcium in the filtrate is precipitated in the usual way by addition of ammonium oxalate and, after strong ignition, weighed as oxide; the magnesium is determined by the addition of ammonium phosphate to the filtrate from the oxalate. (Cf. *infra* under Sulphate.)

5. **Arsenic**, as described above, p. 281.

6. **Carbonic Acid** may be estimated as described under Pyrites (p. 288). This estimation is of some importance, since blende occasionally contains spathic iron ore and calamine, in addition to calcium and magnesium carbonate.

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[1] *Chem. Zeit.*, 1903, **27**, 987.

[2] *Monatsh.*, 1898, **19**, 404.

[3] *Chem. Zeit.*, 1902, **26**, 611.

7. **Fluorine** is determined, according to Prost and Balthaser,[1] by mixing 5 g. of the blende with powdered quartz, heating with sulphuric acid, condensing the liberated silicon fluoride in water, filtering off the separated silica, precipitating the hydrofluosilicic acid with potassium chloride and alcohol, and weighing on a tared filter paper. This method gives results from 0·6 to 0·8 per cent. too low.

Bein[2] estimates the fluorine indirectly, from the silica separated as above. This method is, however, inexact.

Bullnheimer[3] obtained the best results by the following modification of the method of Fresenius.[4] An Erlenmeyer flask of 300 to 350 c.c. capacity is fitted with a rubber stopper, bored in three places, for a thermometer and for inlet- and outlet-tubes respectively. To the last is connected a U-tube filled with glass wool, and beyond this a Winkler cooling worm, which is cooled by immersion in water; a Drehschmidt wash-bottle filled with 80 c.c. of potassium chloride solution is attached to the worm. The inlet-tube is intended, as in the Fresenius method, for admission of air, previously dried and purified by sulphuric acid and soda-lime. About 2·5 g. of the blende are intimately mixed with from 3 to 5 g. of powdered quartz, and treated in the flask with 20 g. of chromic acid and 100 c.c. of concentrated sulphuric acid. Should the chromic acid not be absolutely dry, it must be mixed with the sulphuric acid before adding it to the ore. The flask is quickly stoppered, shaken, and a current of air passed through, at first in the cold, and subsequently with gradual heating to about 80°. When the evolution of oxygen begins to slacken, further heat is applied, until the temperature reaches 150° to 160°; so long as oxygen is coming off, the current of air may be discontinued. The reaction proceeds sometimes quietly, at other times violently. After three hours' heating, all the silicon fluoride should have been driven over into the receiver, and nothing more should be evolved from the absorption flask. The contents of the latter are then emptied out, an equal volume of alcohol added, the mixture allowed to stand for a time, and then titrated with $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. The titration must be done rapidly, and the reading taken at the first reddening of the indicator.

8. **Available sulphur.**—From the total sulphur, estimated as directed on p. 289, there must be deducted :—

for 1 part Pb found in No. 3 : 0·1595 parts S,
" 1 " CaO " 4 : 0·5712 " S,
" 1 " MgO " 4 : 0·7943 " S.

The quantity of sulphur remaining after these deductions is that

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[1] *Z. angew. Chem.*, 1901, **14**, 101.
[2] *Z. anal. Chem.*, 1887, **26**, 733.
[3] *Z. angew. Chem.*, 1901, **14**, 103.
[4] *Quantitative Analysis*, 6th edition (1876), vol. i., p. 328.

available for the production of sulphuric acid. Any sulphur present as heavy spar remains in the insoluble residue from the original extraction.

CONTROL OF WORKING CONDITIONS

The objects to be aimed at in the production of sulphurous acid are (i) the fullest possible utilisation of the raw material employed, and (ii) the correct admixture of air. The former is controlled by the analysis and the appearance of the cinders, and the latter by examination of the products of combustion. Anemometers find but little application at this stage, but may be of great importance during the subsequent conversion of sulphurous acid to sulphuric acid.

I. BURNT ORE.—(Residues after Calcination.)

Crude or native Sulphur.—An analysis is scarcely necessary, since with the small quantity of fixed residue usually present, it is apparent to the eye whether combustion has been complete or not. Should it be deemed desirable, the residue is examined by ignition in a porcelain dish, or by oxidation with aqua regia.

Gas Residuals.—The residues in this case contain iron oxide and frequently lime. The presence of the latter renders a determination of the total sulphur of little value; the available sulphur must be estimated by the method given on p. 270.

Iron Pyrites.—The sulphur in pyrites cinders may exist either as sulphide or as sulphate. In the case of pyrites containing lead or zinc, it is impossible to completely decompose the sulphates of these metals in the kiln, whilst with cupriferous pyrites the complete burning-off of the sulphur is not desirable in view of the subsequent working up of the burnt ore for copper by the "chlorinating roast." In the latter case the burnt ore may contain, according to circumstances, from 3 to 5 per cent. of sulphur, and in the case of mixed pyrites even larger quantities. On the other hand, with pure iron pyrites, the sulphur may be reduced to 1 per cent., at all events in the case of "smalls."

As a rule, only the total sulphur is determined in the burnt ore; in the case of cupreous pyrites the copper is also determined, and less frequently the iron is estimated as well.

Estimation of sulphur. The wet method (p. 272) is seldom employed for this determination, partly because it is more troublesome than in the case of the ore, and also because rapid dry methods which are available are sufficiently accurate (*cf.* p. 276). If the cinders are intended for use in blast furnaces, Jene[1] states that the dry methods of determination should always be used, as the wet methods do not give the total sulphur; this has been confirmed by Gottlieb.[2] Many of

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[1] *Chem. Zeit.*, 1905, **29**, 362.

[2] *Ibid.*, 1905, **29**, 688.

these are, however, untrustworthy or not sufficiently convenient. This is the case, for example, with the method of Pelouze and also with Kolb's method of ignition with sodium carbonate and oxide of copper.[1]

The method proposed by Böckmann is as follows:—A sample of the burnt ore from the kilns is taken every twelve hours, each kiln being provided with two sample boxes, one large and one small, numbered to correspond to the kiln. The samples are in the first instance collected in the smaller receivers and brought in these to the laboratory, where they are transferred to the corresponding larger boxes. At the end of the week's working a good average sample is drawn from the latter, broken down in an iron mortar, the coarsely ground sample so obtained divided by quartering on a piece of stout paper, and one of the quarters finely ground and sieved. The ground samples are filled into bottles, also numbered to correspond to the kilns. Finally, several grams of each sample are ground in successive small portions in an agate mortar until no grittiness is felt on rubbing between the fingers.

For the sulphur determination 1·5 to 2 g. of the very finely ground material are weighed off, and mixed with about 25 g. of a mixture of six parts sodium carbonate and one part potassium chlorate; this mixing is done in a large platinum dish, by the aid of an agate pestle fixed to a wooden handle. The mixture is then fused over the blowpipe. The melt is allowed to cool till only just warm, then covered with hot water, heated to boiling, and both the solution and the insoluble residue washed into a 250 c.c. flask. The contents are cooled under the tap, made up to the 250 c.c. mark, and $\frac{4}{5}$ of the solution filtered through a pleated filter paper into a 200 c.c. flask. The insoluble portion of the melt (oxides of iron, copper, etc.) only occupies a small volume, and it is unnecessary to make any correction for this. The solution is acidified with hydrochloric acid and the sulphuric acid estimated in the usual manner.

The method devised by Watson[2] is much more rapid than that of Böckmann, but it is unsatisfactory in its original form, owing to the difficulty of preventing the very finely divided oxide of iron from passing through the filter and thereby interfering with the end-reaction of the titration. Lunge[3] has modified the process so as to overcome this difficulty, whereby the method has been rendered convenient and rapid, and accurate to within 0·2 per cent. The Watson-Lunge method is as follows:—

Exactly 2 g. of sodium bicarbonate of known alkalinity are intimately mixed by means of a flattened glass rod with 3·2 g. of the ground cinders in a nickel crucible of 20 to 30 c.c. capacity; the mixture

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, 3rd edition, 1903, vol. i., p. 74.

[2] *J. Soc. Chem. Ind.*, 1888, **7**, 305.

[3] *Z. angew. Chem.*, 1892, **5**, 447.

is heated for ten minutes over a small gas flame the tip of which just touches the bottom of the crucible. The crucible must be covered during this preliminary heating, and the contents must not be disturbed during this period lest some of the material be carried away by the gas evolved. Finally the heating is continued for fifteen minutes over a larger flame; the mixture is stirred frequently during this period, and the temperature must not be allowed to rise sufficiently high to cause fusion.

To prevent absorption of sulphur from the combustion products of the gas, it is best to support the crucible in a hole cut in an obliquely placed asbestos card, as shown in Fig. 106, p. 243. The arrangement proposed by D. Pfeiffer[1] is perhaps preferable. By the action of atmospheric oxygen the sulphur is converted into sulphate at the cost of a corresponding quantity of the bicarbonate. The contents of the crucible are emptied into a porcelain dish, the crucible washed out with water and the solution boiled for ten minutes, with the addition of a saturated solution of sodium chloride; without this addition it is difficult to prevent some oxide of iron passing through the filter paper at a later stage. The insoluble residue is then filtered off and washed until free from alkali, the filtrate cooled, and the unchanged sodium carbonate titrated with normal hydrochloric acid (of which 1 c.c. $=0{\cdot}05305$ g. Na_2CO_3, corresponding to 0·01603 g. S), using methyl orange as indicator. If 2 g. bicarbonate require a c.c. of normal acid and the final solution requires b c.c., then the percentage content of sulphur $=\frac{a-b}{2}$.

The method is not applicable to pyrites containing much zinc (*cf.* p. 298), nor to zinc-free cinders which contain 6 per cent. or more of sulphur. For the latter the following mixture must be substituted for that given above, in order to ensure complete oxidation and at the same time to guard against fusion:[2]—1·603 g. of the sample, 2·0 g. sodium bicarbonate, 4 g. potassium chlorate, and 2 to 3 g. ferric oxide, free from sulphur. The determination is otherwise conducted as above; the sulphur content is $=a-b$.

The sodium chloride employed must be quite pure, that is, not only react perfectly neutral, but also be free from calcium and magnesium chlorides, which, if present, would naturally fix a corresponding quantity of sodium bicarbonate.

At the Duisburg copper works the same method is employed for estimating the sulphur in burnt ore as that described for pyrites (p. 276). In dissolving the substance, however, only a few drops of hydrochloric acid are added to the nitric acid, since with larger amounts of hydrochloric acid sulphuretted hydrogen may occasionally be evolved.

List applies the sodium peroxide method (p. 276) to burnt ore.

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[1] *Chem. Zeit.*, 1904, **28**, 38.

[2] Lunge, *Z. angew. Chem.*, 1906, **19**, 27.

The following process is employed in one of the largest French works for the regular daily control of the calcination; it enables a large number of sulphur tests in burnt ore to be carried out simultaneously, and the results are obtained in a comparatively short time. The method depends upon the fact that at a red heat hydrogen will decompose all sulphur compounds of iron with the formation of sulphuretted hydrogen. The sulphuretted hydrogen so liberated is passed into a standard solution of silver nitrate, and is estimated by titrating back the excess of this reagent according to Volhard's method (p. 123). The test is carried out as follows:—Several porcelain tubes, closed at both ends by non-vulcanised rubber stoppers carrying glass tubes, are arranged in a furnace heated by a six-flamed Bunsen burner. The glass tubes are connected at the inlet end with a hydrogen generator by means of a corresponding number of lengths of rubber tubing furnished with screw clips; the outlet pieces are connected with vertically bent tubes which dip into small test-glasses. The hydrogen used must be freed from any accompanying sulphuretted hydrogen by washing with silver nitrate solution. Each set is numbered, and the porcelain tubes, stoppers, inlet- and outlet-tubes and test-glasses are marked to correspond.

A preliminary test is first made to ensure that no precipitate results when the hydrogen is passed into the silver nitrate solution in the test-glasses. When this has been ascertained, exactly 1 g. of the finely ground cinders is weighed into a numbered porcelain boat, the boat pushed to the marked position in the porcelain tube by means of a glass rod, and 25 c.c. of silver nitrate solution (containing 10·604 g. $AgNO_3$, corresponding to 3·65 g. NaCl per litre) placed in each test-glass. When all the weighed samples are in position a current of hydrogen is passed through the tubes and regulated by means of the screw clips to two to three bubbles per minute. After ten minutes, when all the air has been expelled, the furnace is heated, at first gently, and then gradually raised to a red heat. After one and a half hours' heating, the elimination of the sulphur is complete. This is shown by no further cloudiness appearing in the silver nitrate solution, and by the improved and satisfactory settling out of the black precipitate of silver sulphide. The gas supply to the furnace is then gradually reduced, and the hydrogen current interrupted. The test-glasses are removed in turn, and without filtering off the precipitate, 1 c.c. of iron-indicator (2·5 g. ferric nitrate dissolved in 100 c.c. nitric acid of sp. gr. 1·38) is added, and the solution immediately titrated with ammonium thiocyanate solution to permanent redness. The thiocyanate solution contains 4·752 g. per litre, and should correspond exactly with the silver nitrate solution. If the number of c.c. of ammonium thiocyanate required be denoted by *a*, then the percentage of sulphur in the pyrites cinders is given by the expression $\frac{25-a}{10}$.

Copper is estimated in the Duisburg works as described on p. 285, except that only 1 g. of the sample is employed, and solution effected by hydrochloric acid, to which a few drops of nitric acid have been added. Further, no deduction for bismuth and antimony is made from the weight of copper obtained by electro-deposition.[1]

List[2] ignites 5 g. of the cinders with 5 g. of sodium bicarbonate in an iron crucible, a treatment which renders the iron oxide readily soluble in strong hydrochloric acid. The copper in the solution thus obtained is estimated as described under pyrites (p. 285).

Iron. 0·5 g. of the burnt ore is taken, and the iron brought into solution by prolonged warming with strong hydrochloric acid; the boiling solution is then reduced by zinc free from iron, or, more conveniently, by stannous chloride, any excess of which is removed by the addition of a small quantity of mercuric chloride. The ferrous chloride solution so obtained is poured into 500 c.c. of water, to which have been added about 2 g. of manganese sulphate, coloured pink by one or two drops of potassium permanganate solution. The iron content is arrived at by titration with $N/10$ potassium permanganate solution, of which each 1 c.c. equals 0·0056 g. Fe, or, on 0·5 g. of burnt ore, 1·12 per cent. of iron.

Zinc Blende.—Experiments by Lunge have shown that the Watson-Lunge method (p. 295) for the determination of sulphur in burnt ore is not applicable to roasted blende; subsequent investigations by Lunge and Stierlin[3] have, however, proved that the oxidation can be satisfactorily effected by the addition of potassium chlorate to the sodium bicarbonate. 3·206 g. of the finely powdered and sieved sample are mixed with 2 g. of sodium bicarbonate and 2 g. of finely powdered potassium chlorate and heated for thirty minutes in a nickel crucible over a flame 3 to 4 cm. high, the tip of which is 2 to 3 cm. from the bottom of the crucible; after this interval the heating is continued for a further twenty minutes with a bigger flame, so that the bottom of the crucible is reached by the tip, and finally for ten minutes more with a still stronger flame, so that the bottom of the crucible is red hot, but care being taken that the contents do not fuse. The mass is then extracted and titrated as described under the Watson-Lunge method (p. 295). The method can also be applied to unburnt (green) zinc blende, if 2 g. of sulphur-free oxide of iron be added to the above mixture for the decomposition.

As an alternative the sulphur may be estimated gravimetrically,

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[1] *Cf.* Fresenius, *Z. anal. Chem.*, 1877, **16**, 338.

[2] *Z. angew. Chem.*, 1903, **16**, 416.

[3] *Z. angew. Chem.*, 1906, **19**, 21.

following the method described under raw blende (p. 289). The precipitation of the iron by ammonia may be omitted in the ordinary routine testing at works.

Hassreidter and van Zuylen[1] reduce the sulphates formed with stannous chloride, and estimate the sulphur from the sulphuretted hydrogen obtained, by passing it into brominated hydrochloric acid.

A rough guide to the progress of the calcination consists in treating the calcined ore in a flask with 10 c.c. of hydrochloric acid (1 : 2) and testing the evolved gas with neutral or slightly alkaline lead acetate paper; the extent of the calcination is judged by the degree of darkening obtained.[2] This test is employed by the foreman in the furnace room.

Zinc is estimated as on p. 289.

II. Examination of the Kiln Gases

This examination extended formerly only to the determination of the percentage volume of sulphur dioxide in the gases, and was usually carried out according to Reich's method,[3] the apparatus recommended by Lunge being as a rule employed (cf. *infra*). It has, however, been proved that the kiln gases always contain sulphuric anhydride, which may either be useful, as in the manufacture of sulphuric acid, or harmful, as in the preparation of sulphite liquor for use in the wood-pulp industry. The quantity of sulphur trioxide present may reach 10 per cent. of the sulphur content of the gas, and as it is not estimated in Reich's method of testing, the conclusions drawn as to the properties of the gas from the determination of the sulphur dioxide alone, may be quite erroneous, as has been shown by F. Fischer[4] from other considerations.

Lunge[5] consequently recommends the estimation of the total acidity in the gases, that is, $SO_2 + SO_3$, by passing them through a solution of sodium hydroxide, coloured by phenolphthalein, until the colour disappears, instead of merely passing them through iodine solution. Other indicators are not suitable; phenolphthalein is the only one which indicates the simultaneous formation of sodium sulphite and sodium sulphate from the mixed gases (*cf.* pp. 65 and 72). In the manufacture of sulphuric acid the Lunge test is generally sufficient for works purposes; Reich's test may, however, if desired, be employed in

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[1] *Z. angew. Chem.*, 1905, **18**, 1777; 1906, **19**, 137.

[2] Meyer, *Z. angew. Chem.*, 1894, **7**, 7392.

[3] F. Reich, "*Die bisherigen Versuche zur Beseitigung des schädlichen Einflusses des Hüttenrauches bei den fiskalischen Hüttenwerken zu Freiberg*, Freiberg, 1858." Special reprint from *Berg and Hütten Zeitung; cf.* also Winkler, *Industriegase*, vol. ii., p. 350; and, Lunge, *Sulphuric Acid and Alkali*, vol. i., p. 402.

[4] *Dingl. polyt. J.*, 1885, **258**, 28.

[5] *Z. angew. Chem.*, 1890, **3**, 563.

addition. Both tests should be carried out in the preparation of sulphite liquors, and also when the kiln gases are worked for sulphur trioxide and only the residual sulphur dioxide goes into the lead chambers.

Reich's method for the estimation of Sulphur Dioxide.—The kiln gases are drawn by means of an aspirator through water to which a measured quantity of iodine and starch solutions have been added. The end of the reaction is indicated by the disappearance of the blue colour. The volume per cent. of sulphur dioxide in the gases is calculated from the quantity of iodine solution employed and the volume of water aspirated, this latter being the equivalent of the non-absorbable portion of the gas.

The arrangement of the Reich apparatus, as modified by Lunge, is shown in Fig. 122.

The bottle A has a capacity of about 200 c.c., B a capacity of 1000 c.c. After removal of the rubber stopper *d*, A is filled with distilled water to about a quarter of its capacity, and starch solution, sodium bicarbonate, and sufficient iodine solution to produce a strong blue coloration added. The sodium bicarbonate increases the absorptive capacity of the iodine solution and at the same time overcomes any irregularity likely to occur in the course of the reaction. The bottle B is filled almost completely with water, and the cork *c* is then fitted in the hole specially made in the gas-main for the purposes of the test.

It is first necessary to test whether the apparatus is perfectly tight. With this object the spring clip *m* is closed and the clip *i* opened; the water should then only flow for a very short time. Should the water continue to flow the apparatus is not air-tight, and the leak must be located and repaired.

The rubber tubing *b* and the tube *a* are then filled with the kiln gas to be examined. To effect this the clip *m* is opened and then the clip *i* sufficiently to allow the water to flow slowly out and the gas to enter in single bubbles through *a* and rise to the surface of the liquid. As soon as decoloration takes place the clip *i* is closed and 10 c.c. of $N/10$ iodine solution added through the opening *d*.

Before starting a test, the gas to be examined must first be syphoned to the lower end of the tube *a*, so that the air contained in the vessel A may be at the same pressure as that obtaining in the subsequent operation. This is done by cautiously opening the clip *i* until the kiln gas is drawn to the desired point. This clip is then closed quickly, the water collected in C thrown away, and the measuring cylinder again placed in position. The clip *i* is then opened with the one hand and the flask A shaken with the other until the colour of the solution disappears, when the clip is closed and the volume of the water collected is read.

The reaction proceeds according to the equation :—

$$2I + SO_2 + 2H_2O = 2HI + H_2SO_4.$$

Consequently the 10 c.c. of iodine solution employed (=0·12697 g. I) correspond to 0·03203 g. SO_2, or to 10·93 c.c. of SO_2 measured at 0° and 760 mm. Assuming that 128 c.c. of water have been collected in

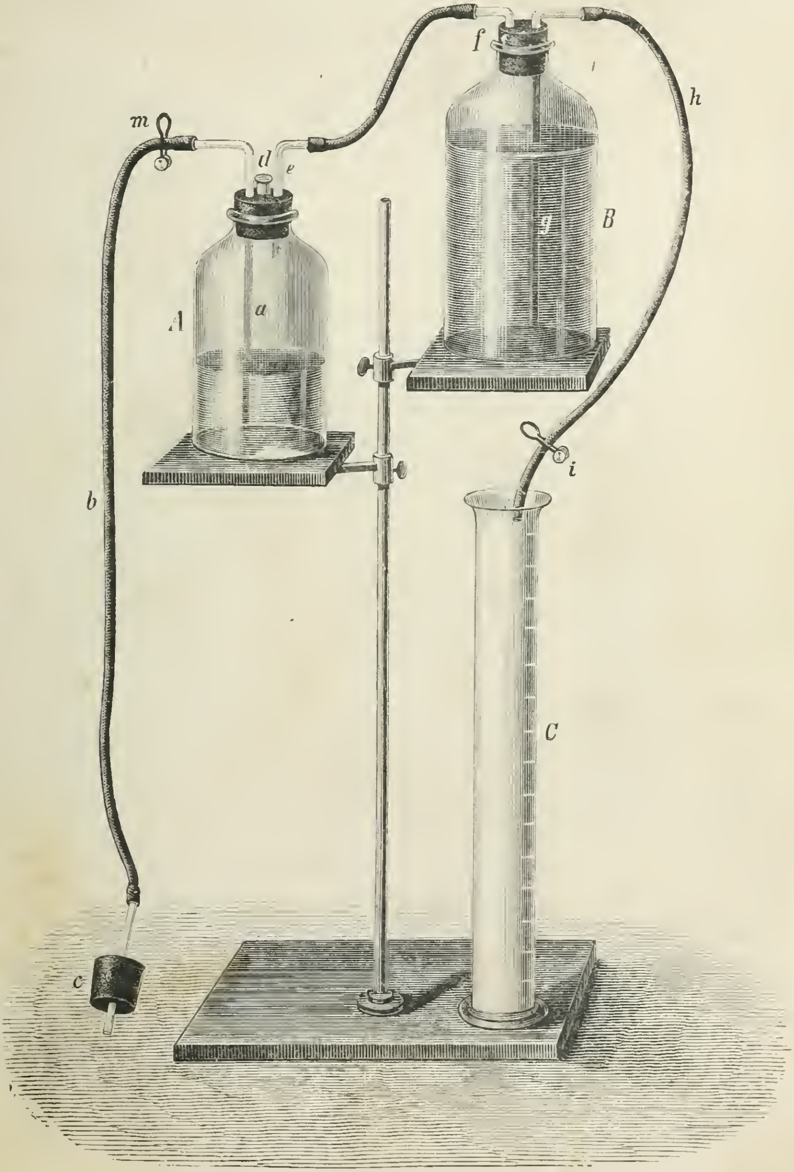

Fig. 122.

any one determination, this corresponds to 128 c.c. of non-absorbable gas drawn through the iodine solution. The total volume of gas aspirated is, therefore, 128 + 10·93 = 138·93 c.c., and the percentage volume of SO_2:—

$$\frac{10.93 \times 100}{138.93} = 8 \text{ per cent.}$$

This calculation is avoided by making use of the following table:—

Cubic Centimetres Water collected.	Volume per cent. SO_2 in Kiln Gas.	Cubic Centimetres Water collected.	Volume per cent. SO_2 in Kiln Gas.
80·1	12	125·7	8
84·1	11·5	134·8	7·5
88·4	11	145·2	7
93·2	10·5	157·2	6·5
98·4	10	171·2	6
104·1	9·5	187·8	5·5
110·5	9	207·8	5
117·7	8·5	...	...

In this table no account is taken of variations in temperature and barometric pressure; should it be desired to correct for these, the volume read off is reduced to 0° and 760 mm. by Tables Nos. VI. to VIII. (Appendix), and the percentage volume of sulphur dioxide taken from the corrected volume by the above table. The necessary addition for the volume of the absorbed gas is included in the table.

Reich's method is not applicable to gases containing more than very small quantities of nitrogen acids. It cannot, for example, be employed in the case of gases leaving the chamber system, since the nitrogen acids contained in these would re-oxidise the hydriodic acid.

Lunge's method for the estimation of Total Acids ($SO_2 + SO_3$).—The above apparatus may be employed, but the glass inlet-tube to the absorption flask should preferably be closed at the bottom, and the portion immersed in the solution pierced with a number of small holes to subdivide the stream of gas (Fig. 123). The gases are conducted through a solution of $N/10$ sodium hydroxide solution coloured with phenolphthalein until the colour is just discharged, the flask being continuously shaken during the absorption. The total acidity is usually calculated to sulphur dioxide by means of the table given above.[1]

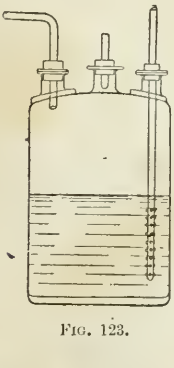

Fig. 123.

Errors may arise with both methods under certain conditions, owing to the presence of arsenious acid, which accumulates in the absorption tube; they are best guarded against by filtering the gases through asbestos.

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[1] For further details, *cf.* Lunge, *Z. angew. Chem.*, 1890, 3, 563.

Lunge employs the absorption bottle shown in Fig. 123, both for this test and for that of Reich. It has a capacity of 410 c.c., and is charged with 230 c.c. of water, 10 c.c. of $N/10$ sodium hydroxide solution, and 3 drops of phenolphthalein solution, for the total acidity determination. The gas is not aspirated continuously, as described above, but intermittently in such fashion that a volume of gas, much smaller than the free space in the bottle, is syphoned over, allowed to stand over the solution, shaken for about half a minute, then a further quantity of gas drawn over, and so on. A longer period of shaking is especially necessary towards the end of the absorption, and it is advisable to place a white ground below the flask to facilitate the observation of the colour change.

In the Thirty-fourth Report of the Inspector for Alkali Works (1897, p. 22), an absorption flask is described which gives good results even in the most difficult cases, such as for example, the absorption of acid fog. It cannot be used for iodine solution, owing to the presence of rubber, but it is very suitable for the Lunge test, for the estimation of hydrochloric acid gas, and in many other cases. The apparatus is shown in Fig. 124 in half the actual size. The flask is fitted with a rubber stopper provided with an inlet- and exit-tube as shown. The former is 8 mm. wide, closed at the bottom, and pierced with a number of small holes, through which the gas passes to the double bulb, which is attached by means of a rubber stopper. The upper bulb is filled with small cuttings of rubber tubing, which are kept in motion by the stream of gas, which is thus brought into very intimate contact with the absorbing solution; the lower bulb is open at the bottom. The success of the apparatus depends largely on the correct dimensions being adhered to. The lower opening of the double bulb is 6 mm. in diameter, the lower bulb 15 mm. and the upper 18 mm. in diameter, and the upper opening through which the inlet-tube passes 13 mm. wide. The gas passes from the bulb into the flask through several small holes, and finally leaves it through the exit-tube, which is narrowed below and widened above to form a cylindrical chamber; the lower, narrow portion is filled with the rubber rings and the upper, wider portion with glass wool. When used for the absorption of acid vapours, the exit-tube is moistened with water coloured by methyl orange, which serves

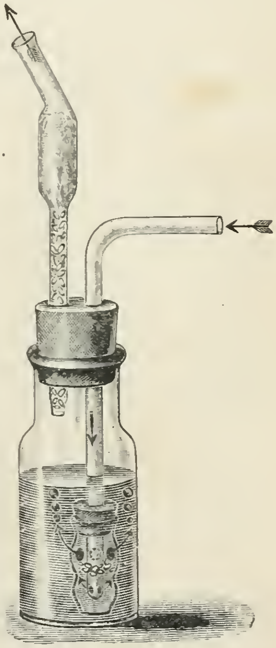
Fig. 124.

to indicate whether complete absorption is being effected in the bottle.

Lunge[1] has proposed to determine the acidity of kiln gases by measuring their specific gravity, a method which might be developed to give a continuous graphic record of the operation of the furnace. Differences of 1 per cent. of sulphur dioxide by volume affect the value of the specific gravity in the second decimal place, those of 0·1 per cent. in the third decimal place. Such measurements might be made by a modification of the Lux gas balance, which, however, as at present constructed is not suitable for use with acid gases, or by the aid of F. C. Müller's[2] method of determining the density of gases. The "Ados" apparatus (*cf.* p. 190) for the examination of flue gases might also be employed; this proposal, however, does not appear to have been worked out.

III. FINISHED PRODUCTS

These comprise, firstly, solutions of sulphurous anhydride in water, which, although seldom appearing on the market, are frequently obtained as intermediate products in many works, as for example, in Hänisch and Schröder's process for the preparation of liquid sulphurous acid; secondly, liquid anhydrous sulphur dioxide; thirdly, the "sulphite liquor" of the wood-pulp industry, a solution of calcium or magnesium sulphite in aqueous sulphurous acid containing more or less sulphuric acid.

Solutions of Sulphurous Acid.—The determination of free sulphurous acid, or of that present as bisulphite, may be made acidimetrically by titration with normal alkali hydroxide solution, bearing in mind the behaviour of the indicator employed. Of the ordinary indicators, litmus is quite unsuitable, phenolphthalein gives the colour change to red, when the normal salt, Na_2SO_3, has been formed, whilst with methyl orange the change to yellow corresponds to the formation of the acid sulphite $NaHSO_3$ (*cf.* p. 65). In the absence of other acids (for example, sulphuric acid, which, if present, may be detected by barium chloride in hydrochloric acid solution), each 1 c.c. of normal alkali used will thus correspond to 0·03203 g. SO_2, when phenolphthalein is used as indicator, and to 0·06406 g. SO_2 when methyl orange is employed. Should free sulphuric acid or other strong mineral acid be present, the sulphurous acid may be determined along with the stronger acid, by titrating two portions, the one with methyl orange, and the second with phenolphthalein as indicator. Less normal alkali will be used in the first than in the second case, in accordance with the behaviour of the two indicators towards sulphurous acid. The difference between the number of the c.c. used in the two cases, multiplied by 0·06406, gives

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[1] *Z. angew. Chem.*, 1890, **3**, 567.

[2] *Ibid.*, 513.

the quantity of free sulphur dioxide in grams; the remaining alkali corresponds to the free strong mineral acid.

An alternative method of estimating free sulphurous acid in the presence of other free non-reducing acids, consists in running the acid into iodine solution, observing the precautions given on p. 113. One c.c. *N*/10 iodine solution corresponds to 0·003203 g. SO_2. Air-freed water must always be used for dilution in this method.

Pure aqueous solutions of sulphurous acid may also be tested by determining the specific gravity; further information on this point will be found in Lunge's *Sulphuric Acid and Alkali*.[1] The following table, published by Giles and Shearer,[2] gives the specific gravities of solutions containing from 0·99 to 13·09 per cent. SO_2.

Specific gravity.	Temp. °C.	Per cent. SO_2.	Specific gravity.	Temp. C.	Per cent. SO_2.
1·0051	15·5	0·99	1·0399	15·5	8·08
1·0102	15·5	2·05	1·0438	15·5	8·68
1·0148	15·5	2·87	1·0492	15·5	9·80
1·0204	15·5	4·04	1·0541	15·5	10·75
1·0252	15·5	4·99	1·0597	12·5	11·65
1·0297	15·5	5·89	1·0668	11	13·09
1·0353	15·5	7·01	...	...	...

Liquid sulphurous acid may be examined in exactly the same way as solutions of sulphurous acid. The contained sulphuric acid may sometimes amount to as much as 20 per cent.[3]

Properties of liquid sulphurous anhydride:[4]—

	At 0°.	At 15°.	At 30°.
Specific gravity . .	1·434	1·391	1·349
Vapour tension . .	1·5	2·7	4·5 Atmos.

One kg. corresponds to a gas volume of 348 litres at 0° and 760 mm. Critical temperature, 155°·4; critical pressure, 78°·9; boiling point, at 760 mm. pressure, − 10°; melting point, − 79°.

Sulphites.—The normal sulphite and the acid sulphite present in sulphites (solid or in solution), may be estimated as follows. The total sulphurous acid is determined by titration with iodine, and the acid sulphite by titration of a second portion with standard alkali and phenolphthalein.

$$\mathrm{NaHSO_3 + NaOH = Na_2SO_3 + H_2O.}$$

One c.c. normal sodium hydroxide solution corresponds to 0·03203 g. SO_2 present as acid sulphite.

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[1] Vol. i., p. 149.

[2] *J. Soc. Chem. Ind.*, 1885, 4, 503.

[3] *Papier Zeit.*, 1892, No. 62.

[4] According to A. Lange, *Taschenb. d. Berl. Bezirksvereins deutscher Chemiker*, 1898-99, p. 82.

If the quantity of sulphurous acid present in a solution exceeds that necessary to form bisulphite, the solution is first titrated with normal sodium hydroxide and methyl orange until the red colour changes, phenolphthalein is then added, and the titration continued till the coloration is formed. Each 1 c.c. of the alkali required with methyl orange corresponds to 0·06406 g. SO_2 in the free condition, and each further c.c. required for the subsequent titration with phenolphthalein to 0·06406 g. SO_2 present as $NaHSO_3$, or half this quantity = 0·03203 g. as "half-free" sulphurous acid.

Sulphite Liquors for the manufacture of Wood-pulp.—The following estimations are necessary:—

1. *Total content of sulphurous acid.* The sulphite solution, which usually contains about 50 g. of sulphur dioxide per litre, is preferably diluted to twice its volume and the diluted solution allowed to flow from a burette into 25 c.c. of an acidified *N*/10 iodine solution until the colour is discharged (*cf.* p. 116). The volume of the iodine solution employed oxidises 0·080075 g. SO_2, consequently the volume of sulphite liquor used for the titration contains this total amount of free and fixed sulphur dioxide.

2. *Content of half-free and of free sulphurous acid*, that is, all sulphur dioxide over and above that required for the formation of calcium sulphite and which is present in the half-free condition as acid sulphite or as free sulphur dioxide in solution, in the liquor. The quantity present is arrived at by titration with normal sodium hydroxide solution, using phenolphthalein as indicator. Each 1 c.c. alkali used corresponds to 0·03203 g. SO_2 in the half-free or free state.

NITRIC ACID MANUFACTURE

Chili saltpetre is the only raw material employed in this industry, which is dealt with in this section. Sulphuric acid and the testing of the various waste acids from the manufacture of nitrobenzene, nitroglycerin, pyroxylin, etc., which are frequently used in the nitric acid industry, are described in a subsequent section.

CHILI SALTPETRE

Chili saltpetre should contain at least 95 per cent., and the better qualities 96 to 98 per cent. of sodium nitrate. In addition to this there may occur potassium nitrate,[1] occasionally up to 9 per cent., sodium chloride, sodium sulphate, sodium iodate, sodium perchlorate, and

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[1] *Cf.* Lunge, *Chem. Ind.*, 1886, **9**, 269; Hagen, *Chem. Zeit.*, 1891, **15**, 1528; and, *Z. angew. Chem.*, 1893, **6**, 495 and 698.

insoluble matter; also, in exceptional instances, sodium carbonate, magnesium sulphate, and salts of the heavy metals.

Of these substances the following are usually only tested for qualitatively.

Potassium detected by platinic chloride.

Iodates. According to Beckurts,[1] the solution is acidified with nitric acid and potassium iodide starch solution added; the method will detect $\frac{1}{100}$ mg. of iodic acid in 1 g. nitre. Or the iodic acid may be reduced by zinc and the iodine liberated by heating with strong sulphuric acid, the solution diluted and shaken with carbon bisulphide, which will extract any iodine present, giving a rose-red solution.

Bromine, under similar conditions, colours the carbon bisulphide yellow to reddish yellow.

Sodium perchlorate, the presence of which was first recognised by Beckurts,[2] and has since been repeatedly confirmed, is, according to van Breukeleeven,[3] most easily detected by a micro-chemical test. This is carried out by adding a little rubidium chloride to a few drops of a concentrated filtered solution of the saltpetre placed on a glass slide. Permanganate is added to the solution to the production of a wine-red colour, and the solution evaporated till single crystals form, when the object glass is placed under the microscope and examined to see whether, in addition to the colourless crystals of sodium nitrate, the reddish-violet crystals of rubidium perchlorate are also present. H. Fresenius and Bayerlein[4] recommend this method.

COMMERCIAL ASSAY OF SALTPETRE

In commercial dealings in Chili saltpetre an indirect method of valuation has been generally employed until quite recently, and is still used to a considerable extent for the large shipments to England and to Hamburg.

According to this method only the percentages of moisture, sodium chloride, sodium sulphate, and matter insoluble in water are determined, the sum of these being called the *refraction;* it is assumed that all the rest is actual nitrate. This method[5] cannot in any way be looked upon as accurate, and may lead to considerable error.

For example, the method quite overlooks any potassium nitrate which may be present (*cf.* p. 306), and which, even in refined nitre, may reach several per cent. Since the nitrate is employed for the manufacture of nitric acid, explosives, etc., the higher nitrogen content of sodium nitrate as compared with that of the potassium compound is

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[1] *Pharm. Centr.*, 1886, 233.

[2] *Fischer's Jahresber.*, 1886, 305.

[3] *Chem. Centr.*, 1898, I., 960.

[4] *Z. anal. Chem.*, 1898, **37**, 501.

[5] *Cf.* Alberti and Hempel, *Z. angew. Chem.*, 1892, **5**, 101.

the chief consideration, and it cannot be a matter of indifference to the manufacturer whether he, for instance, receives 9 per cent. potassium nitrate in place of 9 per cent. sodium nitrate, or whether a lot which, according to the analytical results shows 96 to 97 per cent. of sodium nitrate, on testing with the nitrometer is found to contain only 94 to 95 per cent. In addition, the "refraction method" also includes as nitrate any perchlorate which is present.

Complete Analysis, with exception of the Determination of Nitrate and Perchlorate

Moisture.—0·8 g. of the well-mixed and coarsely powdered sample is weighed into a platinum crucible, and cautiously heated over a small flame, so as to just fuse the nitrate; with a little practice it is easy to hit off this point exactly without it being necessary to observe the temperature. The crucible and contents are then allowed to cool in a desiccator and weighed; the heating is repeated at the same temperature, to make certain that constant weight has been reached.

Or 10 g. of the nitrate are dried in the air-bath at 130°, until the weight is constant.

Insoluble Matter.—Fifty g. of the saltpetre are weighed into a beaker on a balance turning to 0·05 g. The sample is dissolved in water and filtered through a filter paper previously tared against a similar paper (p. 28); the washed residue and the tare are then dried together and weighed.

Should the insoluble residue appear to contain appreciable quantities of organic matter, the latter is determined approximately by igniting the filter paper and insoluble residue. The previous drying of the residue is, in this case, preferably done at a higher temperature, say 120° to 130°, since otherwise there will always be a small difference between the weight obtained by drying at 100° and that got by ignition, even in samples perfectly free from organic matter.

Chlorine, Sulphuric acid, Calcium, Magnesium, and Sodium carbonate.—Five g. of the sample are placed in a filter paper standing over a 500 c.c. flask, and dissolved by addition of boiling water; any sand remaining on the filter after washing is complete, is ignited and weighed. The filtrate when cold is made up to 500 c.c., and of this solution 50 c.c. are taken for the determination of chlorine by titration or precipitation with silver nitrate (p. 123), the result being calculated to sodium chloride. A further 50 c.c. are heated to boiling, and precipitated with barium chloride, the resulting barium sulphate filtered off, weighed, and calculated to calcium sulphate. To estimate the calcium and magnesium, 20 g. of saltpetre are dissolved in 1000 c.c. of boiling water, and the calcium estimated by the addition of ammonium oxalate to 500 c.c. of this solution, the magnesium in the remaining 500 c.c. by addition of ammonium phosphate. The sodium carbonate is obtained either by difference, or by dissolving 20 g. of the sample in water, making up to 1000 c.c., and treating 100 c.c. of this solution with sulphuric acid, evaporating to dryness, and igniting until the weight of the residue is constant. The sodium carbonate is calculated from the weight of sulphate so obtained, after making allowance for the calcium and magnesium sulphates present. Any potassium present must also be allowed for.

Potassium.—Potassium was formerly estimated indirectly by converting the bases into sulphates, but the method leads to very uncertain results when, as in this case, one of the constituents is present in only very small proportion.

A much more exact method consists in repeated evaporation of the saltpetre with strong hydrochloric acid and precipitation with platinic chloride, as described in the section on "Potassium Salts."

The potassium is calculated to potassium nitrate, one hundred parts of which are equivalent to 84·09 parts $NaNO_3$.

The Estimation of Nitrate

Numerous methods, of very unequal value, have been proposed for the estimation of nitric acid in saltpetre. These are grouped together in the following list as arranged by Böckmann, with several additions of recent date; it is essentially a summary, and does not make any pretence to be complete.

I. Methods depending on Reduction to Nitric Oxide.

A. *By measurement of nitric oxide.* 1. Lunge's nitrometric method (p. 315; Literature, p. 132).

2. The method of Schlösing-Grandeau[1] as improved by P. Wagner[2] (p. 317).

B. *Volumetric determination of the nitric acid obtained on oxidising nitric oxide with hydrogen peroxide.* Wilfahrth's method.[3]

C. *Reduction by ferrous salts and subsequent titration with permanganate solution.* Method of Pelouze and Fresenius.

II. Reduction to Ammonia in Alkaline Solution.

There are many modifications of this method, of which the following may be mentioned:—

1. Stutzer's method.[4] Reduction by sodium hydroxide and aluminium

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[1] *Agrikulturchem. Analyse*, p. 31.

[2] *Chem. Zeit.*, 1883, **7**, 1710; 1884, **8**, 475.

[3] *Z. anal. Chem.*, 1888, **27**, 411.

[4] *Z. angew. Chem.*, 1890, **3**, 695.

wire. Aluminium prepared by the old method of manufacture is the only kind suitable, and this has ceased to be an article of commerce.

2. Sievert's method.[1] Reduction with zinc dust and iron powder in alcoholic potassium hydroxide solution.

III. Reduction to Ammonia in Acid Solution.

1. Ulsch's method.[2] Reduction by ferrum reductum, and dilute sulphuric acid with subsequent distillation, after rendering alkaline with sodium hydroxide solution. The method is described on p. 311.

2. Schmitt's method.[3] Reduction by a mixture of zinc and iron dust in acetic acid solution.

3. Hildesheimer's modification[4] of Jodlbauer's method. Reduction with phenolsulphuric acid, zinc dust, and mercury.

4. Förster's method.[5] Reduction with sulphosalicylic acid, sodium thiosulphate, and mercury.

5. Ulsch's electrolytic method.[6]

6. Ingham's electrolytic method.[7]

IV. Reduction to Nitrous Acid.

Gantter's method.[8] Reduction by phosphorous acid, and measurement of the nitrogen evolved on heating the resulting ammonium nitrite.

V. Estimation of Nitric Acid by means of the Hydrogen Deficit.

Ulsch's method.[9] A measured quantity of sulphuric acid is allowed to act on strongly coppered iron alone and, separately, upon the couple together with the nitrate solution; the hydrogen evolved in the two cases is measured in the nitrometer and the volumes compared.

VI. Decomposition with Hydrochloric Acid.

1. Förster's method.[10] Two to 3 g. of the saltpetre, dried at 150°, are evaporated with 25 c.c. of 19 per cent. hydrochloric acid three times successively in a roomy porcelain crucible on the water-bath, and the resulting chloride dried at 150° and weighed. The nitrogen equals the loss in weight of the dried saltpetre × 0·5283.

2. Gowan's method.[11] Decomposition with hydrochloric acid and

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[1] *Cf.* Fricke, *Z. angew. Chem.*, 1891, 4, 240.

[2] *Chem. Centr.*, 1890, II., 926; *Z. angew. Chem.*, 1891, 4, 241.

[3] *Chem. Zeit.*, 1890, **14**, 1410; *Z. angew. Chem.*, 1891, 4, 240.

[4] Sullwald, *Chem. Zeit.*, 1890, **14**, 1674.

[5] *Chem. Zeit.*, 1889, **13**, 229; 1890, **14**, 1674.

[6] *Z. Elektrochem.*, 1897, **3**, 546.

[7] *J. Amer. Chem. Soc.*, 1904, **26**, 1241.

[8] *Z. anal. Chem.*, 1895, **34**, 25.

[9] *Ibid.*, 1891, **30**, 175.

[10] *Chem. Zeit.*, 1890, **14**, 509.

[11] *Chem. News*, 1891, **63**, 245; *Z. angew. Chem.*, 1891, 4, 557.

absorption of the resulting nitrosyl chloride and chlorine in potassium iodide:—

$$HNO_3 + 3HCl = Cl_2 + NOCl + 2H_2O. \qquad (1\ HNO_3 = 3Cl).$$

3. Bohlig's method.[1] Decomposition with sulphuric and hydrochloric acids, absorption of the liberated chlorine in potassium ferrocyanide, and subsequent titration with permanganate.

4. Bensemann's method.[2]

VII. Ignition Methods.

1. Chromate method } These methods are described on pp. 318
2. Silica method } and 319.

VIII. Combustion Methods with Soda Lime and other additions (analagous to Will and Varrentrapp's method).

1. Arnold's method.[3] Ignition with soda lime, sodium thiosulphate, and sodium formate.

2. Houzeau's method.[4] Ignition with soda lime, sodium thiosulphate, and sodium acetate.

3. Boyer's method.[5] Ignition with soda lime, calcium oxalate, and sulphur.

IX. Precipitation by "Nitron."

Busch's method.[6] "Nitron" is the name given to the base 1 : 4 diphenyl, 3 : 5 endanilodihydrotriazole; it forms a nitrate which is almost insoluble in water and which is suited for the detection and determination of nitric acid.

This summary of the better-known methods for the determination of nitric acid is included on account of the importance in industrial and agricultural chemistry of an exact determination of the nitrate in saltpetre. More detailed accounts of Ulsch's method, Lunge's nitrometric method, Wagner's improved form of the Schlösing-Grandeau method, and of the methods depending on ignition with potassium chromate and quartz respectively, are given below.

Detailed description of the Chief Methods for the Determination of the Nitrate in Saltpetre

Ulsch's Method, as modified by Böckmann.

The modifications relate to the size of the flask used for the reduction and for the subsequent distillation; to more effective air-

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[1] *Z. anal. Chem.*, 1900, **39**, 498.

[2] *Z. angew. Chem.*, 1906, **19**, 471.

[3] *Chem. Zeit.*, 1885, **9**, 715.

[4] *Ibid.*, 998.

[5] *Comptes rend.*, 1891, **113**, 503.

[6] *Ber.*, 1905, **38**, 856 and 861; *J. Soc. Chem. Ind.*, 1905, **24**, 291; Gutbier, *Z. angew. Chem.*, 1905, **18**, 494.

cooling, and avoidance of other methods of cooling in the distillation; to dispensing with the special bulb-tube intended to prevent alkaline solution being carried into the distillate; to rendering a back titration unnecessary; to the construction of the absorption vessel; to the quantity of the absorbing solution, and to the strength of the sulphuric acid used for titration.

Also, the weights of sample taken for analysis, of sulphuric acid for decomposition of iron powder, and of sodium hydroxide solution employed by Ulsch and Fricke are doubled. These latter changes had previously been recommended by Alberti and Hempel.[1] The essential features of Ulsch's method remain unchanged.

The following solutions are required for the determination:—1 Dilute sulphuric acid (1 : 2). 2. Sodium hydroxide solution of sp. gr. 1·25, absolutely free from nitrogen compounds. 3. $N/5$ sulphuric acid or $N/5$ hydrochloric acid prepared as described on p. 86.

Twenty g. of each of the well-mixed average samples, ground somewhat further in a porcelain mortar, are weighed out, dissolved in water, and the solutions made to 1000 c.c.; 50 c.c. (= 1·0 g. saltpetre) of each solution are then run into a round-bottomed flask of at least 1 litre capacity. The neck of the flask should be at least 10 c.c. long, and of an internal diameter of 2¾ to 3 cm. One g. ferrum reductum is added to the contents of each flask, and then 20 c.c. of the diluted sulphuric acid (1 : 2); as a precaution, an ordinary glass funnel is placed in the neck of each. The funnel is not absolutely necessary, since, with flasks of the dimensions given, any loss by spurting during the violent evolution of gas is almost impossible. When the gas evolution has either ceased altogether or has become very slow, it is accelerated by placing the flasks on sheets of asbestos and heating by a small flame, so that the solutions reach a quiet boil in about four minutes; boiling is then maintained for about a further six minutes, at the end of which time the reduction should be complete.

The flasks are then allowed to cool slightly, in order that the subsequent addition of water shall not crack the funnels, and after the addition of about 150 c.c. of water, the solution is made alkaline by the addition of 50 c.c. of the sodium hydroxide solution prepared as above. At the same time a rapid rotary motion is given to the contents of the flask, and any syrupy material adhering to the upper walls of the flask is washed down by the aid of a wash-bottle. A pinch of zinc dust is then added to each flask, and distillation carried out as follows:—The distilling flask is placed on a sheet of asbestos card, supported on an ordinary tripod, and the neck fitted with a rubber stopper, through which a bent delivery tube passes for the escape of the gas; Lunge

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[1] *Z. angew. Chem.*, 1891, 4, 398.

recommends the use of a bulb-tube. The vertical portion of this tube should have a length of 14 to 15 cm., of which a good 10 to 12 cm. is outside the stopper, whilst the downward portion leading to the absorption dish should be about 7 cm. long, and connected by a piece of rubber tubing about 10 cm. long to a second tube which dips into the absorption dish, care being taken that the two tubes are held flush together. This second tube is continued for about 7 cm. in the same direction as the downwardly bent portion of the exit-tube from the distilling flask, and is then bent at right angles and continued for a length of 50 to 60 cm., when it dips into the absorption dish. This is an ordinary earthenware dish, of about 800 c.c. capacity; it is charged with about 250 c.c. of distilled water to which about two drops of a somewhat strong solution of litmus have been added; the solution should be tinged a rather faint but distinct blue. A drop of the standard sulphuric acid is then added to the contents of the absorption vessel from a burette standing over the latter, and the solution is tested for neutrality by a piece of sensitive litmus paper (p. 79). When the solution is neutral, which may necessitate the addition of a further drop of acid, the burette is filled with acid to the zero mark and the flask heated; the contents, although thick and coloured greenish brown, owing to separation of ferrous and ferric hydroxides, distil quietly and without bumping. Four distillations can be easily carried out simultaneously, and due attention be given to the necessary additions of acid from the burette. Should the nitrate content be approximately known, as is frequently the case in works, so that 90 per cent. of the acid required for titration may be added at the start, six distillations can be attended to at the same time.

Instead of the Böckmann absorption vessel, Lunge prefers a Peligot or other similar tube, in which the gas inlet-tube does not dip into the acid used for absorption (*cf.* Fig. 125, p. 315); this avoids the risk of the acid being drawn back into the distilling flask.

As soon as the acid solution has been neutralised by the ammonia evolved in the distillation, any further ammonia that comes over is clearly indicated by blue stream lines rising from the mouth of the inlet-tube through the reddish-coloured solution. The latter soon assumes a bluish-red colour, unless fresh acid is added from the burette. Even should this take place, there will be no loss of ammonia, provided that fresh acid be added at once, always taking care to maintain the solution as nearly neutral as possible by testing with sensitive litmus paper. Towards the end of the operation, the solution in the absorption vessel becomes appreciably warm, but no loss of ammonia need be feared on this account. Finally, when no further addition of standard acid from the burette has been necessary for several minutes, the inlet-tube is removed from the absorption vessel and, after making certain by the smell that the steam coming off is quite free from ammonia, the distillation is interrupted.

With a distilling flask of the dimensions given, the surface of the liquid is about 18 cm. below the gas exit-tube, and there is consequently no danger of alkaline liquor being carried forward from the flask; in fact the water condensing on the inner end of the exit-tube always shows a neutral reaction, as may readily be proved at the end of the distillation.

Using $N/5$ sulphuric or hydrochloric acid, each 1 c.c. corresponds to 0·01702 g. $NaNO_3$, 0·02024 g. KNO_3, 0·01081 g. N_2O_5, or 0·01261 g. HNO_3. One g. pure $NaNO_3$ consequently requires 58·75 c.c. of $N/5$ acid.

Böckmann recommends the use of burettes of 100 c.c. capacity graduated to $\frac{1}{10}$ c.c.; this, however, necessitates a very inconvenient length. His proposal to use burettes of this capacity and graduated to $\frac{1}{20}$ c.c. is quite unpractical. Any great error in gauging the quantity of sulphuric acid to be added may be avoided by making the other determinations (refraction determination and potassium estimation, if necessary) prior to the nitrogen test. Should these indicate that more than 50 c.c. of acid are requisite, the full burette content of 50 c.c. may be run into the absorption vessel before beginning the distillation, the burette refilled, and the distillation started.

If the burette be read to 0·05 c.c., or preferably to 0·025 c.c., the total error will not exceed ± 0·1 per cent. of the nitrate if due precautions are taken. This degree of accuracy can, however, only be attained after considerable practice.

Vogtherr[1] recommends the apparatus described below (Fig. 125) for carrying out this test. It was primarily designed for nitrogen determinations by Kjeldahl's method, in which the digestion with sulphuric acid is carried out without the use of a fume chamber, and in the same apparatus as is used for distilling off the ammonia, and serves also for the estimation of ammonia in ammonium sulphate and analogous determinations.

A Jena glass Kjeldahl flask is fitted above with a glass bell accurately ground in so as to be gas-tight, the bell being continued as a glass tube bent first in a slightly inclined downward direction and then vertically. The vertical portion is connected by a cork or rubber stopper with a bulb-tube the lower open end of which dips below the solution in the absorption flask. The long neck and the glass bell prevent spurting of the liquid from the reaction flask, the pear-shaped bulb prevents the sucking back of the liquid used for absorption, whilst the cork or rubber connections employed are reduced to a minimum.

A drawback to this otherwise very satisfactory method lies in the

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[1] *Chem. Zeit.*, 1902, **27**, 988.

fact that commercial ferrum reductum is not always sufficiently pure, and according to Brandt,[1] errors amounting to as much as 0·8 per cent. may arise from this cause.

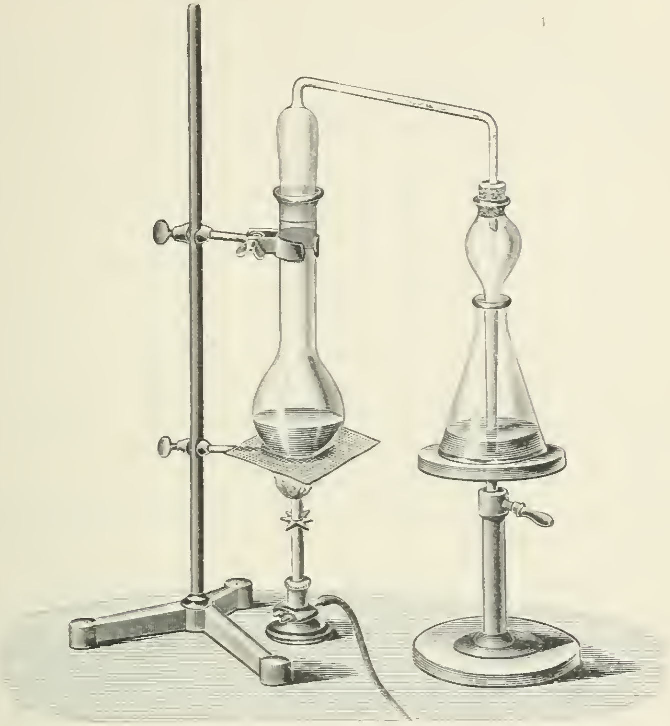

FIG. 125.

Lunge's Nitrometric method.—The principle of this method, which is due to W. Crum, was first rendered practically available by the introduction of Lunge's "nitrometer" (p. 132). The method depends on the fact that nitric acid, nitrous acid and their salts and esters, when brought into intimate contact with mercury and a large excess of sulphuric acid are decomposed quantitatively, so as to yield the whole of their nitrogen in the form of nitric oxide, the volume of which is measured. The reaction is:—

$$2HNO_3 + 3H_2SO_4 + 6Hg = 2NO + 3Hg_2SO_4 + 4H_2O.$$

In the analysis of saltpetre the bulb nitrometer (Fig. 45, p. 136) may be employed. It is preferable, however, to carry out the decomposition of the nitre with mercury and sulphuric acid in a special decomposition vessel, as shown in Fig. 52 (p. 144), so that the gas measurement can be made over dry mercury. The decomposition may be effected in the

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[1] *Chem. Zeit.*, 1899, **23**, 22.

ordinary simple nitrometer, taking note of temperature and barometric pressure, and reducing the gas volume obtained to normal (0° and 760 mm.), but it is more convenient to employ the gas volumeter (p. 138), which allows the corrected gas volume to be read directly.

The quantity of nitre taken for the determination must be such that, under the conditions of temperature and barometric pressure obtaining at the time, not less than 100 c.c. and not more than 120 c.c. of nitric oxide are evolved. This corresponds to about 0·35 g., a quantity which has given rise to much adverse criticism of the method. So far as such criticism relates to the accuracy of the actual determination it may be dismissed, since a gas volume of over 100 c.c. is obtained, and this volume can be read off with ease to 0·05 c.c. or even less, which means an accuracy of at least 1 in 2000. This degree of accuracy is not obtainable by any other method. There is more reason, however, in the contention that a correct average sample cannot well be obtained when so small a quantity as 0·35 g. is taken for the analysis. This objection may be overcome if, as recommended by J. Stroof, 20 g. of the nitre, dried at 110°, are thoroughly ground, and the exact average sample taken from this again dried to constant weight.

When the bulb nitrometer without a decomposing vessel is employed, the operation is carried out as follows. The well-mixed finely powdered sample, obtained as above described, is filled into a narrow, marked weighing tube, and the tube corked and weighed. When filled to the mark, the tube should contain about 0·35 g. substance. The contents are then shaken into a previously prepared "saltpetre nitrometer," that is, one of at least 130 c.c. capacity (p. 136), so that the powder falls as far as possible on to the bottom of the glass cup. During this operation the three-way cock must be in such a position that none of its passages are open either above or at the side. About half a c.c. of water is then poured in, and allowed to stand a short time until the nitre is completely or nearly dissolved, when the solution and crystals are drawn into the measuring tube by cautiously opening the tap and lowering the levelling tube; the cup is washed out with ½ or at most 1 c.c. of water, and about 15 c.c. of strong pure sulphuric acid admitted to the tube. If too much water is employed, that is, more than 1½ c.c. in all, the sulphuric acid is rendered too dilute and a persistent froth containing basic mercuric sulphate, is formed which causes difficulty in reading. The reaction is brought about by thoroughly shaking the acid solution with the mercury. The levelling tube is then placed approximately at its correct height so as to avoid any great difference of pressure and consequent error owing to leakage, and the apparatus allowed to cool for at least half an hour. The tubes are then accurately levelled, allowing one division of mercury for each six and a half divisions occupied by the acid solution in the measuring tube, and the gas volume read off. To test whether the gas is actually under atmospheric pressure, a few drops of sulphuric acid are poured into the cup, and allowed to flow into the measuring tube by cautiously opening the tap as described on p. 135.

The temperature and barometric height are read at the same time and the gas volume reduced to 0° C. and 760 mm. pressure by means of the tables. Each 1 c.c. NO corresponds to 0·0037986 g. $NaNO_3$; the total volume x divided by the weight a taken and multiplied by 100 gives the percentage content, which is thus $= \frac{0·37986x}{a}$.

The nitrometer must, of course, be accurately graduated, and the operator should satisfy himself that the readings are correct.

By this method it is easy to obtain results agreeing to within 0·2 per cent. Still greater accuracy may be attained with practice, certainly to at least 0·1 per cent., by using a separate decomposing vessel and transferring the gas to the measuring tube as described on p. 143. The manipulation is much cleaner when working in this way; also several decomposing vessels may be operated at the same time and all the gas volumes read off in a single measuring tube.

If a gas volumeter be employed, the reduction tube must, of course, be set for dry gas, or if set for moist gas, the operation must be carried out as described on p. 141, most conveniently by sucking a tiny drop of water into the gas measuring tube.

Baskerville and Miller[1] have stated that mercury is attacked at ordinary temperatures by sulphuric acid of sp. gr. 1·84 with the formation of sulphur dioxide, and that this may give rise to errors in nitrometric work. Pitman[2] has shown that this objection is groundless, and this has since been admitted by the above authors;[3] they now state that such action only occurs with acid of 99 per cent. strength and not with acid of 94 to 95 per cent., such as is generally used for laboratory work.

The view that the solubility of nitric oxide in the resulting solutions may lead to appreciable error has been disproved by Lunge,[4] Nernst and Jellinek,[5] Tower,[6] and by Newfield and Marx.[7]

The Schlösing-Grandeau-Wagner Method.

This method depends upon the reduction of nitric acid to nitric oxide, which is collected and measured.

The apparatus required for the determination consists of a flask of 250 to 300 c.c. capacity, closed by a double-bored rubber stopper and furnished with a tap funnel of 15 c.c. capacity. The lower end of the

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[1] *Chem. Centr.*, 1898, **I.**, 85.
[2] *Ibid.*, 1898, **I.**, 709.
[3] *Ibid.*, 1898, **II.**, 89.
[4] *Ber.*, 1885, **18**, 1391; 1886, **19**, 111. *Chem. News*, 1886, **53**, 289.
[5] *Z. anorg. Chem.*, **49**, 219 and 236.
[6] *Ibid.*, **50**, 382.
[7] *J. Amer. Chem. Soc.*, 1906, **28**, 877.

funnel-tube, which is fused together so as to contract the outlet, reaches to the middle of the flask, but not to the solution. A tube, suitably bent to dip into a glass dish containing well-boiled water, passes through the second opening in the stopper and serves as the exit-tube for the liberated gas. The measuring tube, which is preferably provided with a glass tap at its upper end and graduated from the top downwards in $\frac{1}{10}$ c.c., is supported above the dish in a clamp. Forty c.c. of ferrous chloride solution, containing 400 g. per litre, and an equal volume of well-boiled 10 per cent. hydrochloric acid, are introduced into the flask and the contained air expelled from the apparatus by continued boiling, care being taken that the funnel-tube always contains hydrochloric acid. When all air has been expelled the gas exit-tube is placed in position below the measuring tube and 10 c.c. of a normal saltpetre solution, containing exactly 33 g. pure sodium nitrate per litre, is introduced into the funnel-tube. The tap is then turned so as to allow this solution to flow drop by drop into the boiling ferrous chloride solution. When all but a small volume has been introduced the funnel is washed out twice with 10 per cent. hydrochloric acid, which, like the nitrate solution, is added drop by drop to the boiling solution in the flask. The operation is finished when the evolution of nitric oxide ceases. About 90 c.c. of nitric oxide should result under the foregoing conditions. The measuring tube is removed and, supported by a small dish containing water, cautiously transferred to a correspondingly tall glass cylinder filled with water. A second measuring tube is then brought into position and, without interrupting the boiling, a measured volume of a solution of the nitre to be tested is introduced and treated as above described, and so on with a third, fourth, and further tests as required. When the several tubes have attained the temperature of the cooling water the volume of nitric oxide in each is read off, after raising the tube so as to bring the water inside and outside to the same level. The content of each solution is obtained by comparing the gas volumes evolved from the sample and from the standard solution respectively. When carried out in this manner the method is very simple, and may be recommended; it requires, however, careful manipulation.

According to Liechti and Ritter,[1] who have thoroughly investigated Schlösing's method, good results are obtained even in the presence of organic matter, for which purpose it was originally worked out; this has, however, been disputed by R. Pfeiffer.[2]

Method by Ignition with Potassium Chromate or with Silica.

To the dried 0·8000 g. of substance used for the moisture determination (p. 308) are added approximately 3 g. of a previously fused and, after cooling, finely ground mixture of equal parts of bichromate and

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[1] *Z. anal. Chem.*, 1903, **42**, 1.

[2] *Ibid.*, 612.

neutral chromate of potassium, and the whole heated, at first gradually and finally more strongly till the mass melts uniformly. The loss in weight = N_2O_5. This method can only be used if the sample is quite free from alkaline carbonates. An alternative method is to ignite a mixture of 2 g. of the salt with about seven times its weight of ignited silica free from carbonates, for from two to four hours at a good red heat.

Pauli[1] recommends this method, but Alberti and Hempel[2] together with most other authorities do not consider it sufficiently trustworthy. The method cannot be employed in the presence of perchlorate.

The conclusions drawn by Alberti and Hempel, and which have been amply corroborated, are :—

1. The indirect method of examining Chili saltpetre ("refraction" determination), at present very generally employed, should be abolished. The results obtained are extremely inaccurate, and the method cannot be justified from the chemical standpoint.

2. The direct methods of determining the nitrogen in Chili saltpetre by means of Lunge's nitrometer, by the process of Schlösing and Grandeau as improved by Wagner, and by Ulsch's method, give accurate results, and the introduction of one of these methods is to be advocated.

3. In the case of Chili saltpetre intended for agricultural use, the results should be expressed on the basis of the nitrogen content only; calculation to sodium nitrate is incorrect, and should only be made exceptionally and under reserve.

4. In saltpetre intended for industrial use, the impurities should be estimated in addition to the nitrogen, and an exact analysis, taking account of the potassium compounds present, is necessary.

ESTIMATION OF PERCHLORATE

Sodium perchlorate is directly injurious in many of the applications of saltpetre. It occurs practically in all shipments of Chili nitre, and its presence must always be taken into account. A method for its qualitative detection has been described on p. 307.

All methods for the estimation of the perchlorate are based on a determination of the chlorine present as chloride in the sample, the conversion of perchlorate to chloride in a second portion of the material, followed by a determination of the total chlorine then present as chloride; the difference between the two tests represents the perchlorate.

The conversion of the perchlorate to chloride may be effected by simply heating for a sufficient length of time, whereby the oxygen of any perchlorate present is driven off.

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[1] *J. Soc. Chem. Ind.*, 1897, **16**, 494.

[2] *Z. angew. Chem.*, 1892, **5**, 103.

Sjollema[1] and Freytag[2] have given detailed instructions for carrying out the estimation on this principle.

According to Selckmann,[3] the method is both slow and uncertain, and he recommends fusing 5 to 10 g. of the nitre, the chloride content of which has been determined, with three to four times its weight of lead shavings in a porcelain crucible of 40 to 50 c.c. capacity, gradually increasing the heat, and stirring with a copper wire; finally, after ten to fifteen minutes heating, raising the temperature until the bottom of the crucible is at a dark red heat, at which it is maintained for one to two minutes. The melt is then soaked in hot water, the lead chloride decomposed by warming with sodium bicarbonate or hydroxide solution, the solution filtered, and the chlorine estimated gravimetrically as silver chloride.

Hönig[4] finds that good results may be obtained with finely divided iron (ferrum limatum). Two to 3 g. of the iron are added to 5 to 10 g. of the fused nitre, in a nickel crucible, and the mixture heated for half an hour without bringing the temperature of the crucible to appreciable redness.

Erck[5] proposes to first decompose the chloride by boiling with nitric acid of sp. gr. 1·4, and alcohol, and then to convert the perchlorate into chloride by ignition.

Winteler[6] has pointed out various sources of error in the earlier methods. He finds that fuming nitric acid will quantitatively reduce perchlorate to chloride at 200° in a sealed tube. Any chloric acid originally present must, however, be removed by evaporation with hydrochloric acid.

O. Förster[7] recommends the following method as universally applicable. Ten g. of the nitre, the chloride content of which is known, are mixed with an equal quantity of sodium carbonate, free from chlorine, and heated in a covered platinum dish, or in a roomy porcelain crucible over the full flame until the melt becomes perfectly fluid and only small bubbles are given off; this should be effected in ten minutes. The product is then dissolved in nitric acid, and the chloride estimated in the usual manner.

Blattner and Brasseur[8] first estimate the chlorine present as chloride, and then heat a mixture of 5 to 10 g. of the nitre and 8 to 15 g. of calcium hydroxide, free from chlorine, over a Bunsen burner for fifteen minutes, allow to cool, dissolve in nitric acid, and estimate the total chlorine by any suitable method. Calcium hydroxide is to be preferred to an alkaline carbonate or hydroxide, on account of the greater ease in manipulation.

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[1] *Chem. Zeit.*, 1896, **20**, 1002.

[2] *Chem. Centr.*, 1898, **I.**, 1203; *Z. angew. Chem.*, 1898, **11**, 1021.

[3] *Z. angew. Chem.*, 1898, **11**, 101.

[4] *Chem. Zeit.*, 1903, **27**, 32.

[5] *Ibid.*, 1897, **21**, 21.

[6] *Ibid.*, 75.

[7] *Ibid.*, 1898, **22**, 357.

[8] *Ibid.*, 589.

Various authorities recommend an addition of native peroxide of manganese (pyrolusite) for the better decomposition of the perchlorate. This was first proposed by Hellich.[1] Ahrens and Hett[2] heat the nitre with sodium carbonate and chlorine-free manganese dioxide, to facilitate the decomposition of the perchlorate, to fusion and redness, treat the solution of the melt with nitric acid and potassium permanganate to permanent coloration, and estimate the chloride by Volhard's method.

C. Gilbert, in a brochure entitled *Methoden zur Bestimmung des Perchlorats* (Tubingen, 1899), gives the following directions for carrying out the pyrolusite method:—Twenty-five g. of nitre are dissolved in water, made up to 250 c.c., and the chloride determined by titrating 50 c.c. of the filtered solution with silver nitrate (1 c.c. = 0·01 g. NaCl) and potassium chromate (see p. 123). A second 25 g. of the nitre, preferably after the addition of 2·5 g. of the purest powdered pyrolusite (Merck's), is heated for half an hour at 540° in an air-bath in a nickel crucible fitted with a deep concave lid, and having a capacity of 70 c.c. The aqueous solution of the melt is then made up to 250 c.c., filtered, and the chlorine again determined as above. The air-bath recommended is that designed by Lothar Meyer; it will hold from three to six crucibles, and should be fitted with a gas regulator and a Le Chatelier pyrometer or thermometer reading up to 570° (p. 174). Dupré[3] proceeds in essentially the same manner, omitting, however, the pyrolusite, but heating 20 g. of the sample for one hour at 545° in an air-bath of the type recommended by Gilbert. Instead of a pyrometer, a covered nickel crucible may be used in which is placed a platinum crucible, resting on a layer of asbestos paper, and containing about 1 g. of potassium perchlorate. By observing, after the completion of the heating, whether the residue in the platinum crucible fuses without any appreciable evolution of gas, a gauge of the temperature employed is obtained. The chloride may also be determined by Volhard's method (p. 123), or gravimetrically.

Should iodate be present, Ahrens and H. Gilbert effect the fusion with addition of sodium carbonate. Twenty g. of the dried nitrate are thoroughly moistened with 2 to 3 c.c. of a concentrated solution of sodium carbonate, 1 g. of pyrolusite added, the mixture dried and maintained in a state of fusion at a low red heat for fifteen minutes. The solution of the melt is then oxidised with potassium permanganate solution, and the chlorine determined by Volhard's method.

Recently, sodium chlorate as well as perchlorate has been detected in Chili saltpetre, and methods for its estimation have been devised. In the examination of 107 samples of nitre, Märcker[4] found the percentage of perchlorate present to vary from 0·27 to 5·64, with a mean value of 0·94 per cent., and in addition 0·1 to 1·0 per cent. of chlorate, as

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[1] *Chem. Zeit.*, 1894, **18**, 485.

[2] *Chem. Centr.*, 1898, **II.**, 558; *Z. angew. Chem.*, 1898, **11**, 1020.

[3] *J. Soc. Chem. Ind.*, 1902, **21**, 825.

[4] *Chem. Centr.*, 1898, **II.**, 925.

determined by the method then in vogue. The presence of perchlorate is regarded as objectionable in nitre intended for agricultural purposes, and although the practical investigation into the extent of the injury it may cause has not yet been concluded, it has been suggested that the maximum quantity to be allowed should not exceed 1½ per cent.

Mennicke[1] estimates a mixture of chloride, chlorate, and perchlorate in the following manner. (*a*) The nitre is ignited with addition of alkali hydroxide or carbonate to convert all the chlorine compounds to chloride, which is determined. (*b*) Chloride and chlorate are estimated by gently boiling 5 g. of the nitre with 10 g. of zinc dust (free from chlorine), and 150 c.c. of 1 per cent. acetic acid for half an hour, filtering and determining the chloride. (*c*) The chloride originally present in the nitre is determined directly. This method has shown the presence of appreciable quantities of chlorate.

Blattner and Brasseur[2] treat a solution of 5 to 10 g. of the nitrate with excess of sulphurous acid, either as gas or in solution, thereby reducing only the chlorate and not the perchlorate, drive off the excess of sulphur dioxide by boiling, and saturate the warm solution with calcium carbonate. The chloride is estimated in the cold, filtered solution in the ordinary manner, and the chlorine present in the sample as chlorate is obtained by deducting from this value that of the chloride originally present in the nitre. The total chlorine is determined by igniting the saltpetre with calcium hydroxide as described above, and the perchlorate arrived at by difference.

Arnould[3] has described the following method, which is employed in the French Government laboratory. The chloride originally present is precipitated by the addition of neutral silver nitrate solution and filtered off; the chlorate in the filtrate is reduced by warming this to 90°, and adding an excess of lead nitrite, prepared by simply shaking lead nitrite with water and without filtering; any cloudiness due to the nitrite is removed by the addition of a few drops of dilute nitric acid. If any opalescence persists after this treatment, chlorate is present, and the amount is estimated by comparison with similarly prepared solutions to which known quantities of chlorate have been added. For the French powder factories it is specified that the nitre must contain less than 0·01 per cent. chloride, 0·01 per cent. chlorate, and 0·1 per cent. perchlorate.

Lemaitre[4] reduces the perchlorate by fusion with sodium sulphite; this method has been improved by Fschernobojew,[5] who has shown that chlorate can be determined simultaneously.

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[1] *Chem. Zeit. Rep.*, 1898, **22**, 117.

[2] *Ibid.*, 1900, **24**, 793.

[3] *Mémorial des poudres et salpêtres*, 1902.

[4] *Monit. Scient.*, 1904, **18**, 253; *Chem. Centr.* 1904, **I.**, 1427.

[5] *Chem. Zeit.*, 1906, **29**, 442.

CONTROL OF WORKING CONDITIONS

The process control in the manufacture of nitric acid consists essentially in the determination of the yield and of the quality of the nitric acid. In addition, care must be taken that no nitrogen oxides escape into the chimney or into the atmosphere; the tests applied are similar to those employed in the sulphuric acid industry (*cf.* p. 336).

The bisulphate drawn from the retort must also be examined; this is done in the following manner:—

1. *Free acid* is estimated by titration with normal sodium hydroxide solution. In the presence of considerable amounts of iron oxide or of alumina no indicator is added, and the titration is considered finished as soon as the first signs of a permanent flocculent precipitate appear.

2. *Nitric acid* may be determined in the nitrometer or gas volumeter as in the nitrometric method for the estimation of saltpetre. The acid sulphate is dissolved in the minimum quantity of water in the cup above the tap, and decomposed with a large excess of sulphuric acid (pp. 137 and 139). Since the quantity of nitric acid present in acid sulphate is always small, a nitrometer either with a narrow measuring tube as used in the examination of acids, or with a central bulb (Fig. 46, p. 136), should be employed.

NITRIC ACID

Pure, absolute nitric acid, HNO_3, is very difficult to prepare, and scarcely keeps any length of time, owing to the liberation of oxygen with formation of hyponitric acid, which latter causes the colourless acid to turn yellow or, with larger quantities of nitrogen peroxide, red. The boiling point is 86°, the specific gravity at $\frac{15^\circ}{4^\circ}$ slightly above 1·52.

The hydrates of nitric acid have been especially studied by Küster and Kremann.[1]

The strongest commercial acid has, when pure and almost free from nitrogen peroxide, a sp. gr of 1·50 or slightly higher, corresponding to 94 to 95 per cent. HNO_3. It begins to boil a little above 86°, the boiling point rising as distillation proceeds, owing to more acid than water distilling over, until 126° is reached, at which temperature an acid containing 68·9 per cent. HNO_3, and having a sp. gr. 1·42 distils over unchanged. Weaker acids have again a lower boiling point, and yield on distillation, with a continual rise in temperature, more water than acid until the boiling point 126° is attained, when acid of the above composition distils over.

Lunge and Rey's[2] investigations into the relationship between the

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[1] *Z. anorg. Chem.*, 1904, **40**, 1.

[2] *Z. angew. Chem.*, 1891, 4, 165.

specific gravity and percentage content of nitric acid solutions have led to the older tables, such as that of Kolb, being superseded. The following table is based on their researches. The specific gravity determinations made by Winteler[1] have been shown to be unreliable by Lunge[2] by Veley and Manley,[3] and by Pützer.[4] Values agreeing with those of Lunge and Rey within, at the outside $\frac{1}{300}$ ($\frac{1}{240}$ in one case only), have been obtained by Veley and Manley,[5] who add that greater concordance is scarcely to be expected between different observers employing different methods.

An additional table (p. 327) for correcting the specific gravity obtained at higher or lower temperatures to the normal value, viz. the specific gravity of the acid at 15°, compared with water at 4° as the unit,[6] is also given.

This table has been worked out for pure acids, and the values do not apply absolutely to observations made on commercial acids, which are never pure. In the cases of sulphuric and hydrochloric acids, except for the highest strengths, such differences are not great; they may, however, be considerable in the case of commercial nitric acid, owing to the presence of lower oxides of nitrogen, generally calculated to hyponitric acid. The influence of hyponitric acid on the specific gravity has been observed by many investigators,[7] but no method has been

Specific Gravity of Initial Acid 1·4960 *at* 15°/4° (in vacuo).

N_2O_4 per cent.	Alteration of the Specific Gravity by N_2O_4.	N_2O_4 per cent.	Alteration of the Specific Gravity by N_2O_4.	N_2O_4 per cent.	Alteration of the Specific Gravity by N_2O_4.
0·25	0·00050	4·50	0·02875	8·75	0·05825
0·50	0·00075	4·75	0·03050	9·00	0·06000
0·75	0·00150	5·00	0·03225	9·25	0·06160
1·00	0·00300	5·25	0·03365	9·50	0·06325
1·25	0·00475	5·50	0·03600	9·75	0·06500
1·50	0·00675	5·75	0·03775	10·00	0·06600
1·75	0·00775	6·00	0·03950	10·25	0·06815
2·00	0·01050	6·25	0·04175	10·50	0·06975
2·25	0·01250	6·50	0·04300	10·75	0·07135
2·50	0·01425	6·75	0·04475	11·00	0·07300
2·75	0·01625	7·00	0·04650	11·25	0·07450
3·00	0·01800	7·25	0·04720	11·50	0·07600
3·25	0·01985	7·50	0·05000	11·75	0·07750
3·50	0·02165	7·75	0·05165	12·00	0·07850
3·75	0·02350	8·00	0·05325	12·25	0·08050
4·00	0·02525	8·25	0·05500	12·50	0·08200
4·25	0·02690	8·50	0·05660	12·75	0·08350

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[1] *Chem. Zeit.*, 1905, **29**, 689 and 1009.

[2] *Ibid.*, 1905, **29**, 689 and 1072.

[3] *Ibid.*, 1905, **29**, 1270.

[4] *Ibid.*, 1905, **29**, 1221.

[5] *J. Soc. Chem. Ind.*, 1903, **22**, 1228.

[6] *Cf.* Fuchs, who has published a detailed table, *Z. angew. Chem.*, 1898, **11**, 747.

[7] Loring Jackson and Wing, *Chem. Zeit. Rep.*, 1887, **11**, 293; and, R. Hirsch, *Chem. Zeit.*, 1888, **12**, 911.

Table of the Specific Gravity of Nitric Acid of various strengths at 15° C. referred to Water at 4° C.

Spec. Grav. at $\frac{15°}{4°}$ (*in vacuo*).	Degrees Beaumé.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains kg.				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.	N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·000	0	0	0·08	0·10	0·19	0·16	0·10	0·001	0·001	0·002	0·002	0·001
1·005	0·7	1	0·85	1·00	1·89	1·61	1·03	0·008	0·010	0·019	0·016	0·010
1·010	1·4	2	1·62	1·90	3·60	3·07	1·95	0·016	0·019	0·036	0·031	0·019
1·015	2·1	3	2·39	2·80	5·30	4·52	2·87	0·024	0·028	0·053	0·045	0·029
1·020	2·7	4	3·17	3·70	7·01	5·98	3·79	0·033	0·038	0·072	0·061	0·039
1·025	3·4	5	3·91	4·60	8·71	7·43	4·72	0·040	0·047	0·089	0·076	0·048
1·030	4·1	6	4·71	5·50	10·42	8·88	5·64	0·049	0·057	0·108	0·092	0·058
1·035	4·7	7	5·47	6·38	12·08	10·30	6·54	0·057	0·066	0·125	0·107	0·068
1·040	5·4	8	6·22	7·26	13·75	11·72	7·45	0·064	0·075	0·142	0·121	0·077
1·045	6·0	9	6·97	8·13	15·40	13·13	8·34	0·073	0·085	0·161	0·137	0·087
1·050	6·7	10	7·71	8·99	17·03	14·52	9·22	0·081	0·094	0·178	0·152	0·096
1·055	7·4	11	8·13	9·84	18·64	15·89	10·09	0·089	0·104	0·197	0·168	0·107
1·060	8·0	12	9·15	10·68	20·23	17·25	10·95	0·097	0·113	0·214	0·182	0·116
1·065	8·7	13	9·87	11·51	21·80	18·59	11·81	0·105	0·123	0·233	0·198	0·126
1·070	9·4	14	10·57	12·33	23·35	19·91	12·65	0·113	0·132	0·250	0·213	0·135
1·075	10·0	15	11·27	13·15	24·91	21·24	13·49	0·121	0·141	0·267	0·228	0·145
1·080	10·6	16	11·96	13·95	26·42	22·53	14·31	0·129	0·151	0·286	0·244	0·155
1·085	11·2	17	12·64	14·74	27·92	23·80	15·12	0·137	0·160	0·303	0·258	0·164
1·090	11·9	18	13·31	15·53	29·41	25·08	15·93	0·145	0·169	0·320	0·273	0·173
1·095	12·4	19	13·99	16·32	30·91	26·35	16·74	0·153	0·179	0·339	0·289	0·184
1·100	13·0	20	14·67	17·11	32·41	27·63	17·55	0·161	0·188	0·356	0·304	0·193
1·105	13·6	21	15·34	17·89	33·89	28·89	18·35	0·170	0·198	0·375	0·320	0·203
1·110	14·2	22	16·00	18·67	35·36	30·15	19·15	0·177	0·207	0·392	0·335	0·212
1·115	14·9	23	16·67	19·45	36·84	31·41	19·95	0·186	0·217	0·411	0·350	0·223
1·120	15·4	24	17·34	20·23	38·31	32·67	20·75	0·195	0·227	0·430	0·366	0·233
1·125	16·0	25	18·00	21·00	39·77	33·91	21·54	0·202	0·236	0·447	0·381	0·242
1·130	16·5	26	18·66	21·77	41·23	35·16	22·33	0·211	0·246	0·466	0·397	0·252
1·135	17·1	27	19·32	22·54	42·69	36·40	23·12	0·219	0·256	0·485	0·413	0·263
1·140	17·7	28	19·98	23·31	44·15	37·65	23·91	0·228	0·266	0·504	0·430	0·273
1·145	18·3	29	20·64	24·08	45·61	38·89	24·70	0·237	0·276	0·523	0·446	0·282
1·150	18·8	30	21·29	24·84	47·05	40·12	25·48	0·245	0·286	0·542	0·462	0·293
1·155	19·3	31	21·94	25·60	48·49	41·35	26·26	0·254	0·296	0·561	0·478	0·304
1·160	19·8	32	22·60	26·36	49·92	42·57	27·04	0·262	0·306	0·580	0·494	0·314
1·165	20·3	33	23·25	27·12	51·36	43·80	27·82	0·271	0·316	0·598	0·510	0·324
1·170	20·9	34	23·90	27·88	52·80	45·03	28·59	0·279	0·326	0·617	0·526	0·334
1·175	21·4	35	24·54	28·63	54·22	46·24	29·36	0·288	0·336	0·636	0·543	0·345
1·180	22·0	36	25·18	29·38	55·64	47·45	30·13	0·297	0·347	0·657	0·560	0·356
1·185	22·5	37	25·83	30·13	57·07	48·66	30·90	0·306	0·357	0·676	0·577	0·366
1·190	23·0	38	26·47	30·88	58·49	49·87	31·67	0·315	0·367	0·695	0·593	0·376
1·195	23·5	39	27·10	31·62	59·89	51·07	32·43	0·324	0·378	0·715	0·610	0·388
1·200	24·0	40	27·74	32·36	61·29	52·26	33·19	0·333	0·388	0·735	0·627	0·398
1·205	24·5	41	28·36	33·09	62·67	53·23	33·94	0·342	0·399	0·755	0·644	0·409
1·210	25·0	42	28·99	33·82	64·05	54·21	34·69	0·351	0·409	0·775	0·661	0·419
1·215	25·5	43	29·61	34·55	65·44	55·18	35·44	0·360	0·420	0·795	0·678	0·431
1·220	26·0	44	30·24	35·28	66·82	56·16	36·18	0·369	0·430	0·815	0·695	0·441
1·225	26·4	45	30·88	36·03	68·24	57·64	36·95	0·378	0·441	0·835	0·712	0·452
1·230	26·9	46	31·53	36·78	69·66	59·13	37·72	0·387	0·452	0·856	0·720	0·466
1·235	27·4	47	32·17	37·53	71·08	60·61	38·49	0·397	0·463	0·877	0·748	0·475
1·240	27·9	48	32·82	38·29	72·52	61·84	39·27	0·407	0·475	0·900	0·767	0·487
1·245	28·4	49	33·47	39·05	73·96	63·07	40·05	0·417	0·486	0·921	0·785	0·498
1·250	28·8	50	34·13	39·82	75·42	64·31	40·84	0·427	0·498	0·943	0·804	0·511

Table of the Specific Gravity of Nitric Acid, etc.—*Continued.*

Spec. Grav. at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees Beaumé.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains kg.				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.	N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·255	29·3	51	34·78	40·58	76·86	65·54	41·62	0·437	0·509	0·965	0·822	0·522
1·260	29·7	52	35·44	41·34	78·30	66·76	42·40	0·447	0·521	0·987	0·841	0·534
1·265	30·2	53	36·09	42·10	79·74	67·99	43·18	0·457	0·533	1·009	0·860	0·547
1·270	30·6	54	36·75	42·87	81·20	69·23	43·97	0·467	0·544	1·031	0·879	0·558
1·275	31·1	55	37·41	43·64	82·65	70·48	44·76	0·477	0·556	1·054	0·898	0·570
1·280	31·5	56	38·07	44·41	84·11	71·72	45·55	0·487	0·568	1·077	0·918	0·583
1·285	32·0	57	38·73	45·18	85·57	72·96	46·34	0·498	0·581	1·100	0·938	0·596
1·290	32·4	58	39·39	45·95	87·03	74·21	47·13	0·508	0·593	1·123	0·957	0·608
1·295	32·8	59	40·05	46·72	88·48	75·45	47·92	0·519	0·605	1·146	0·977	0·621
1·300	33·3	60	40·71	47·49	89·94	76·70	48·71	0·529	0·617	1·169	0·997	9·633
1·305	33·7	61	41·37	48·26	91·40	77·94	49·50	0·540	0·630	1·193	1·017	0·646
1·310	34·2	62	42·06	49·07	92·94	79·25	50·33	0·551	0·643	1·218	1·038	0·659
1·315	34·6	63	42·76	49·89	94·49	80·57	51·17	0·562	0·656	1·243	1·059	0·673
1·320	35·0	64	43·47	50·71	96·05	81·90	52·01	0·573	0·669	1·268	1·080	0·686
1·325	35·4	65	44·17	51·53	97·60	83·22	52·85	0·585	0·683	1·294	1·103	0·701
1·330	35·8	66	44·89	52·37	99·19	84·58	53·71	0·597	0·697	1·320	1·126	0·715
1·3325	36·0	66·5	45·26	52·80	100·00	85·27	54·15	0·603	0·704	1·333	1·137	0·722
1·335	36·2	67	45·62	53·22	100·80	85·95	54·58	0·609	0·710	1·346	1·148	0·728
1·340	36·6	68	46·35	54·07	102·41	87·32	55·46	0·621	0·725	1·373	1·171	0·744
1·345	37·0	69	47·08	54·93	104·04	88·71	56·34	0·633	0·739	1·400	1·193	0·758
1·350	37·4	70	47·82	55·79	105·67	90·10	57·22	0·645	0·753	1·427	1·216	0·772
1·355	37·8	71	48·57	56·66	107·31	91·51	58·11	0·658	0·768	1·455	1·240	0·788
1·360	38·2	72	49·35	57·57	109·03	92·97	59·05	0·671	0·783	1·483	1·265	0·803
1·365	38·6	73	50·13	58·48	110·75	94·44	59·98	0·684	0·798	1·513	1·289	0·818
1·370	39·0	74	50·91	59·39	112·48	95·91	60·91	0·698	0·814	1·543	1·314	0·835
1·375	39·4	75	51·69	60·30	114·20	97·38	61·85	0·711	0·829	1·573	1·339	0·850
1·380	39·8	76	52·52	61·27	116·04	98·95	62·84	0·725	0·846	1·603	1·366	0·868
1·3833	40·0	...	53·08	61·92	117·27	100·00	63·51	0·735	0·857	1·623	1·383	0·879
1·385	40·1	77	53·35	62·24	117·88	100·51	63·84	0·739	0·862	1·633	1·392	0·884
1·390	40·5	78	54·20	63·23	119·75	102·12	64·85	0·753	0·879	1·665	1·420	0·902
1·395	40·8	79	55·07	64·25	121·68	103·76	65·90	0·768	0·896	1·697	1·447	0·919
1·400	41·2	80	55·97	65·30	123·67	105·46	66·97	0·783	0·914	1·731	1·476	0·937
1·405	41·6	81	56·92	66·40	125·75	107·24	68·10	0·800	0·933	1·767	1·507	0·957
1·410	42·0	82	57·86	67·50	127·84	109·01	69·23	0·816	0·952	1·803	1·537	0·976
1·415	42·3	83	58·83	68·63	129·98	110·84	70·39	0·832	0·971	1·839	1·568	0·996
1·420	42·7	84	59·83	69·80	132·19	112·73	71·59	0·849	0·991	1·877	1·600	1·016
1·425	43·1	85	60·84	70·98	134·43	114·63	72·80	0·867	1·011	1·915	1·633	1·037
1·430	43·4	86	61·86	72·17	136·68	116·55	74·02	0·885	1·032	1·955	1·667	1·058
1·435	43·8	87	62·91	73·39	138·99	118·52	75·27	0·903	1·053	1·995	1·701	1·080
1·440	44·1	88	64·01	74·68	141·44	120·61	76·59	0·921	1·075	2·037	1·736	1·103
1·445	44·4	89	65·13	75·98	143·90	122·71	77·93	0·941	1·098	2·080	1·773	1·126
1·450	44·8	90	66·24	77·28	146·36	124·81	79·26	0·961	1·121	2·123	1·810	1·150
1·455	45·1	91	67·38	78·60	148·86	126·94	80·62	0·981	1·144	2·167	1·848	1·173
1·460	45·4	92	68·56	79·98	151·47	129·17	82·03	1·001	1·168	2·212	1·886	1·198
1·465	45·8	93	69·79	81·42	154·20	131·49	83·51	1·023	1·193	2·259	1·927	1·224
1·470	46·1	94	71·06	82·90	157·00	133·88	85·03	1·045	1·219	2·309	1·969	1·250
1·475	46·4	95	72·39	84·45	159·94	136·39	86·62	1·068	1·246	2·360	2·012	1·278
1·480	46·8	96	73·76	86·05	162·97	138·97	88·26	1·092	1·274	2·413	2·058	1·307
1·485	47·1	97	75·18	87·70	166·09	141·63	89·95	1·116	1·302	2·466	2·103	1·335
1·490	47·4	98	76·80	89·60	169·69	144·70	91·90	1·144	1·335	2·528	2·156	1·369
1·495	47·8	99	78·52	91·60	173·48	147·93	93·95	1·174	1·369	2·593	2·211	1·404
1·500	48·1	100	80·65	94·09	178·19	151·96	96·50	1·210	1·411	2·672	2·278	1·447

Table of the Specific Gravity of Nitric Acid, etc.—*Continued.*

Spec. Grav. at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees Beaumé.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains kg.				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.	N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·501	...	...	81·09	94·60	179·16	152·78	97·03	1·217	1·420	2·689	2·293	1·456
1·502	...	...	81·50	95·08	180·07	153·55	97·52	1·224	1·428	2·704	2·306	1·465
1·503	...	...	81·91	95·55	180·96	154·31	98·00	1·231	1·436	2·720	2·319	1·473
1·504	...	...	82·29	96·00	181·81	155·04	98·46	1·238	1·444	2·735	7·332	1·481
1·505	48·4	101	82·63	96·39	182·55	155·67	98·86	1·244	1·451	2·748	2·343	1·488
1·506	...	...	82·94	96·76	183·25	156·27	99·27	1·249	1·457	2·759	2·353	1·494
1·507	...	...	83·26	97·13	183·95	156·86	99·62	1·255	1·464	2·773	2·364	1·502
1·508	48·5	...	83·58	97·50	184·65	157·47	100·00	1·260	1·470	2·784	2·374	1·508
1·509	...	...	83·87	97·84	185·30	185·01	100·35	1·265	1·476	2·795	2·384	1·514
1·510	48·7	102	84·09	98·10	185·79	158·43	100·62	1·270	1·481	2·805	2·392	1·519
1·511	...	...	84·28	98·32	186·21	158·79	100·84	1·274	1·486	2·814	2·400	1·524
1·512	...	...	84·46	98·53	186·61	159·13	101·06	1·277	1·490	2·822	2·406	1·528
1·513	...	...	84·63	98·73	186·98	159·45	101·26	1·280	1·494	2·829	2·413	1·532
1·514	...	...	84·78	98·90	187·30	159·72	101·44	1·283	1·497	2·835	2·418	1·535
1·515	49·0	103	84·92	99·07	187·63	160·00	101·61	1·287	1·501	2·843	2·424	1·539
1·516	...	...	85·04	99·21	187·89	160·22	101·75	1·289	1·504	2·848	2·429	1·543
1·517	...	...	85·15	99·34	188·14	160·43	101·89	1·292	1·507	2·854	2·434	1·546
1·518	...	...	85·26	99·46	188·37	160·63	102·01	1·294	1·510	2·860	2·439	1·549
1·519	...	...	85·35	99·57	188·58	160·81	102·12	1·296	1·512	2·864	2·442	1·551
1·520	49·4	104	85·44	99·67	188·77	160·97	102·23	1·299	1·515	2·869	2·447	1·554

Table for the Correction of the observed Specific Gravity of Nitric Acid for differences of Temperature between 13° and 17° C.

Specific Gravity.	Correction for ± 1°.	Specific Gravity.	Correction for ± 1°.
1·000—1·020	±0·0001	1·281—1·310	±0·0010
1·021—1·040	0·0002	1·311—1·350	0·0011
1·041—1·070	0·0003	1·351—1·365	0·0012
1·071—1·100	0·0004	1·366—1·400	0·0013
1·101—1·130	0·0005	1·401—1·435	0·0014
1·131—1·161	0·0006	1·436—1·490	0·0015
1·162—1·200	0·0007	1·491—1·500	0·0016
1·201—1·245	0·0008	1·501—1·520	0·0017
1·246—1·280	0·0009		

devised to allow for its effect when present. Lunge and Marchlewski[1] have shown that Hirsch's view, that 1 per cent. of nitrous acid corresponds to an increase of 0·01 in the specific gravity, is untenable. Their observations gave the following results for the strongest commercially important acid.

The following example, dealing with nitric acid containing nitrous acid, will illustrate the use of these tables. A sample of nitric

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[1] *Z. angew. Chem.*, 1892, **5**, 10.

acid was found to contain 2·93 per cent. N_2O_4, and to have a sp. gr. of 1·4994 at 20°. From the table on p. 327, which may be used without hesitation for temperatures lying somewhat below 13° or above 17°, it will be seen that the specific gravity becomes, at 15°, $1{\cdot}4994 + (0{\cdot}0016 \times 5) = 1{\cdot}5074$. According to the table on p. 324, 0·0180 must be deducted from this weight, for the 2·93 per cent. (or in round figures 3 per cent.) N_2O_4. This gives, therefore, a sp. gr. for the pure acid $= 1{\cdot}5074 - 0{\cdot}0180 = 1{\cdot}4894$. For this value the round figure 1·490 is taken from the table on p. 326, giving 89·60 HNO_3 as the percentage of the sample. If instead of this value, which takes account of the N_2O_4 present, the value (1·5074) obtained by simply correcting for temperature had been taken, the percentage of nitric acid found would have been given as $\frac{97{\cdot}13 + 97{\cdot}50}{2} = 97{\cdot}31$ obtained as the mean of 1·507 with 97·13 per cent. HNO_3 and 1·508 with 97·50 per cent. HNO_3; that is, instead of the correct value 89·60 per cent., the erroneous value of 97·31 per cent.

In the application of these high strength nitric acids for nitration purposes it is customary to regard the whole of the N_2O_4 as inactive, and the table (p. 324) is calculated from this standpoint. It might in many cases be more accurate to regard half of the nitrogen peroxide as active, according to the equation :—

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

In such case a much smaller deduction should be made, and for this a special table might advantageously be drawn up.

Lunge and Marchlewski have endeavoured to prepare similar tables to make allowance for the nitrogen peroxide present in nitric acid solutions of two lower strengths (sp. gr. 1·4509 and 1·4018), which are included in the range of commercial acids. They were not able, however, to obtain concordant results, apparently owing to the partial or complete conversion of the nitrogen peroxide to nitrous and nitric acids; such tables are still less possible for weaker acids (*cf.* p. 329).

Estimation of Nitrogen peroxide (Hyponitric acid).—This estimation for the correction to be applied to the specific gravity reading of high strength nitric acid solutions (*cf.* p. 324) is carried out as follows: —The acid is allowed to flow slowly and in small quantities at a time, from an accurately calibrated burette, into a measured volume of semi-normal potassium permanganate solution (15·820 g. $KMnO_4$ per litre), warmed to 40°, until the colour disappears. The acid should be allowed to stand for some time in the burette before the titration is made, until it has attained the temperature of the room as measured by an accurate thermometer; this is indicated by the volume remaining constant. The burette should be graduated in $\frac{1}{20}$ c.c., and it should be possible to read with certainty to 0·01 c.c. The number of c.c. of acid required to decolorise the permanganate solution, multiplied by the sp. gr. corresponding to the room temperature, gives the weight of acid used, from which the percentage content in N_2O_4 is calculated in the manner described under the estimation of nitrous vitriol (p. 342). Each 1 c.c. $N/2$ permanganate solution corresponds to 0·02300 g. N_2O_4; thus with a consumption of n c.c. permanganate, and m c.c. of the acid under examination, the content in $N_2O_4 = \frac{0{\cdot}02300n}{m}$ g. per c.c. The estimation of the three nitrogen acids in admixture is described in the section on Sulphuric Acid (p. 340).

The Total Acidity is generally determined in practice by the hydrometer only, notwithstanding the great uncertainty inseparable from the method in this particular case (*cf.* p. 324). It may, of course, be determined by titration, and this should be done in all important cases. This estimation can be carried out without difficulty in the case of slightly fuming acids, by either pipetting a quantity of the previously diluted acid or, preferably, by weighing out a portion of the concentrated acid in the bulb-tap pipette used for fuming sulphuric acid (Fig. 134, p. 390). In titrating, attention must be paid to the destructive action of nitrous acid on methyl orange (*cf.* p. 66). In the case of strongly fuming red acids, even the method of weighing in the special pipette fails to give satisfactory results, owing to the impossibility of completely washing out the nitrogen oxides, especially nitric oxide, which are continually evolved from the strong acid. On this account the following directions given by Lunge and Marchlewski should be adopted:—10 c.c. of the acid are allowed to drop slowly, preferably from a burette, into ice-cold water, the solution made up to 100 c.c., and an aliquot part titrated with a very accurately prepared standard sodium hydroxide solution.

The percentage of total nitrogen acids may also be determined in the nitrometer, employing the bulb form (Fig. 45, p. 136), so as to accommodate the larger volume of nitric oxide evolved. The test is carried out exactly as described under the analysis of saltpetre, the quantities taken being 1 c.c. of the acid, measured in an accurate pipette, and 10 c.c. of concentrated sulphuric acid. This method is, however, only employed in cases in which a large proportion of sulphuric acid is already present, as, for example, in nitrating and spent acids.

Other Tests.—*Fixed residue.* This consists chiefly of sodium sulphate with small quantities of oxide of iron, etc., and is estimated by evaporating 50 c.c. of the acid to dryness, in a place protected from dust, igniting, and weighing.

Krauch[1] states that 10 g. of pure nitric acid should leave, on evaporation in a porcelain dish, only a very minute and scarcely weighable residue; on an average he obtained a residue of from 2 to 3 mg. from 50 g. of pure concentrated acid.

Sulphuric acid (Krauch): 10 g. are evaporated to about 1 c.c. in a porcelain dish, the residue dissolved in 30 c.c. of water, the solution transferred to a beaker, heated, and barium chloride added. No sign of a precipitate should appear in the case of acid. nitric. pur., even after standing for some time.

In carrying out this test, it is necessary to bear in mind that the presence of strong nitric acid retards the precipitation; the greater part of the nitric acid must either be removed by evaporation or nearly neutralised by the addition of chemically pure sodium carbonate.

For the quantitative determination of sulphuric acid the solution is rendered nearly neutral by the addition of pure sodium carbonate, and precipitated by barium chloride as described on p. 274. If the acid leaves an appreciable residue on evaporation, this must be taken into account, as it consists mainly of sodium sulphate.

Chlorine. (Krauch): 50 c.c. of distilled water to which a few drops of silver nitrate solution have been added should show no change on the addition of 5 to 10 c.c. of "pure" nitric acid. This method of carrying out the test removes any uncertainty which may arise should the distilled water employed not be absolutely free from chlorine.

For the quantitative estimation, the acid is neutralised with chemically pure sodium carbonate and titrated with silver nitrate solution; a very slightly alkaline reaction is not prejudicial.

Heavy metals and alkaline earths (Krauch): 20 g. are diluted with water and treated with excess of ammonia, ammonium sulphide, and ammonium oxalate. In the case of acid. nitric. pur., no darkening or cloudiness should be formed.

Iron is detected qualitatively by adding potassium thiocyanate to the previously diluted solution; quantitatively, by supersaturating the acid with ammonia, heating for some time, and collecting the precipitated hydroxide on an ash-free filter. Traces of iron are best determined colorimetrically by means of potassium thiocyanate according to the directions given by Lunge[2] (*cf.* p. 381).

Iodine. Krauch states that nitric acid is coloured yellow by the presence of $\frac{1}{200}$ per cent. of iodine, and that it may be identified by shaking the acid with chloroform (Biltz). A yellow coloration may

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[1] *The Testing of Chemical Reagents for Purity*, trans. by J. Williamson and L. W. Dupré, 1903, p. 185.

[2] *Z. angew. Chem.*, 1896, **9**, 3.

also be due to chlorine compounds, and is generally to be ascribed to the presence of lower nitrogen oxides. The iodine is not usually present in the free state, but as iodic acid dissolved in the nitric acid. The oxygen compounds of iodine, as well as iodine itself, are recognised by cautiously adding a very dilute solution of sulphurous acid or a few drops of sulphuretted hydrogen water to the diluted acid and extracting any iodine so liberated by carbon bisulphide, or testing by the addition of starch solution. An excess of sulphurous acid or of sulphuretted hydrogen destroys the reaction.

An alternative method is to treat the solution with chemically pure zinc, which reduces the iodic acid, whilst the nitrous acid formed at the same time liberates iodine from the hydriodic acid produced. The solution is then well shaken with carbon bisulphide.

According to the Pharmaceutical Commission of the German "Apotheker-Verein,"[1] iodine and iodic acid are tested for by shaking the acid, diluted with twice its volume of water, with a small quantity of chloroform; the solvent should not be tinged violet even after the addition of a small piece of zinc to the acid solution.

Beckurts[2] gives the following as the most delicate test for iodine in nitric acid:—1 c.c. of the acid is boiled to remove lower oxides of nitrogen, and to oxidise all the iodine to iodic acid, and 1 c.c. of well-boiled water is then added, followed by a few drops of a solution of potassium iodide and starch in air-free water. A blue coloration indicates the presence of iodine in the original solution; a blank test made with the potassium iodide and pure acid is essential.

EXAMINATION OF NITRATING AND SPENT ACIDS. (MIXTURES OF SULPHURIC ACID, NITRIC ACID, ETC.)

Mixtures of sulphuric and nitric acids are prepared for coal-tar colour works and for explosives factories for nitrating purposes. On the other hand, waste acids are produced in these works, containing in addition to the original components (of which the greater portion of the nitric acid has naturally been utilised) much nitrous acid and a small quantity of organic matter. Such residual acids as contain large amounts of organic matter, and have attained thereby a tarry consistency, as for example the acids from the purification of benzol and petroleum, will not be considered. They contain no nitric acid, and may be very considerably purified from the tarry matter by dilution; the tarry constituents consist, in the main, of pyridine bases, condensed hydrocarbons, etc.

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[1] *Arch. Pharm.*, 1887, 93.

[2] *Fischer's Jahresber.*, 1886, 305.

According to Guttmann, the average composition of spent acid is as follows:—

	From Nitroglycerine.	From Nitrocellulose.	From Nitrobenzene, Picric Acid, etc.
HNO_3 . .	10	10	1
H_2SO_4 . .	70	80	65
H_2O . .	20	10	34
	100	100	100

No notice is taken of lower nitrogen oxides, and of organic matter in these data.

The following constituents are estimated in nitrating and similar mixtures:—

1. **Total Acidity**.—Two to 3 g. are weighed off in the bulb pipette, allowed to flow cautiously into a large volume of water, and the total acid estimated by titration with normal sodium hydroxide solution. Litmus may be used as indicator, but if so, prolonged boiling is necessary; methyl orange may also be employed, notwithstanding the nitrous acid present, if the titration be carried out in the cold and the operation conducted as described on p. 66.

2. **Lower Nitrogen acids** are estimated by allowing the acid to flow into a measured volume of potassium permanganate solution; the method is more fully described under the testing of nitrous vitriol (p. 342; *cf.* also p. 329). They may be calculated to HNO_2 or N_2O_3 or to N_2O_4 (hyponitric acid). The lower nitrogen oxides contained in the strong nitric acid consist mainly of N_2O_4; on mixing with concentrated sulphuric acid this is converted into equimolecular proportions of HNO_3, and of $SO_2(OH)(ONO)$. In the case of N_2O_4, each c.c. of seminormal permanganate solution used corresponds to 0·02300 g. N_2O_4; if therefore x represents the number of c.c. of permanganate taken, y the c.c. of acid required to decolorise this, and s the specific gravity of this acid, then the N_2O_4 content in g. per litre is equal to $\frac{23{\cdot}00\,x}{y}$, or in percentage by weight to $\frac{2{\cdot}300\,x}{ys}$.

3. **Total Nitrogen acids** are estimated in the nitrometer (p. 132). The value found, less that obtained in determination (2), gives the content of nitric acid, and (1) – (3) that of sulphuric acid.

4. **Sulphuric acid**. Two to 3 g. are weighed in the bulb-pipette (Fig. 134, p. 390), transferred to a small porcelain dish, and heated on the water-bath for a half to one hour, a small quantity of water being at the same time added to destroy all nitrosyl-sulphuric acid. The heat-

ing is continued until on shaking the beaker all nitrous smell has disappeared. The removal of the nitric acid is facilitated by occasionally blowing on to the acid and rotating the dish. The contents are then washed into a beaker and titrated with normal or $N/2$ sodium hydroxide and methyl orange; this gives the sulphuric acid only.

Lunge and Berl[1] have shown that this method gives low results, and they recommend the determination of the sulphuric acid by difference, from the total acidity less the total nitrogen acids, as given above.

The sulphuric acid may also be determined by precipitation as barium sulphate, but the above method effects a considerable saving of time, as a large number of samples can be evaporated simultaneously, and then only require to be titrated to complete the analysis.

SULPHURIC ACID MANUFACTURE

RAW MATERIALS

These have already been described under—*Sulphur* (p. 264), *Spent oxide* (p. 279), *Pyrites* (p. 272), *Zinc blende* (p. 289), *Nitre* (p. 306), and *Nitric acid* (p. 323).

CONTROL OF WORKING CONDITIONS

In the manufacture of sulphuric acid by the lead-chamber process, many factors have to be taken into account, and a certain relationship must exist between these for the regular and satisfactory working of the plant. These factors comprise more especially the temperatures in the various parts of the system, the colour of the gases in the chambers, the draughts, the strengths of drip- and bottom-acid, of the Gay-Lussac and Glover acids (also the temperature of the last), the quantity of nitrogen oxides present in the acids, the composition of the gases, etc.

The rules to be observed in, and the conclusions to be drawn from, these observations are fully described in Lunge's *Sulphuric Acid and Alkali*.[2]

This section is restricted to a description of such methods of investigation as are essential to the satisfactory carrying out of the process.

Examination of the Gases

It is necessary to differentiate: *Inlet gases*, *Chamber gases* from various parts of the system, and *Exit gases* beyond the Gay-Lussac tower.

The examination of the inlet gases (kiln gases from the burning of pyrites or blende) has been described under the preparation of

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[1] *Z. angew. Chem.*, 1905, 18, 1687.

[2] Third edition, 1903, p. 675 *et seq.*

sulphurous acid (p. 299). The determination deals solely with the estimation of sulphur dioxide and sulphur trioxide. It is unnecessary to estimate the oxygen accompanying these gases, since it must always, in normal working, be in reciprocal relationship to the sulphur oxides present.

The examination of the gases in the chambers is generally carried out by observing the colour (more particularly in the hind portion of the system and at the exit), the temperature as measured by means of thermometers inserted at different places in the walls of the chambers, and the pressure under which they stand, for which purpose the manometer and anemometer described on pp. 165 *et seq.* may be employed, though frequently this is only done in a very crude manner by removing plugs or lutes.

Generally speaking, a chemical analysis of the chamber gases is not made, and under ordinary working conditions little would be gained from such an analysis, owing to the difficulty of obtaining really average samples; and further, it is unnecessary, since the process can be perfectly controlled by the analysis of the inlet and outlet gases. Should it be desirable in a special and exceptional case to investigate the chamber gases, the methods described under the investigation of the exit gases will be found perfectly satisfactory. For more exact determinations, reference should be made to the methods employed by Lunge and Naef.[1]

The exit gases from the Glover tower are in the first place examined for their content in oxygen, which constitutes one of the most important factors for the regulation of the process in general, and for the setting of the damper in the exit flue in particular. In many of the foreign works this estimation is looked upon as sufficient, but in England, and more recently in Germany, in consequence of the legal restrictions imposed, the gases are also tested for total acidity.

1. **Oxygen.**—The oxygen is estimated by absorption, and measuring the resulting decrease in volume. The absorption is effected either by means of an alkaline solution of pyrogallol, which, however, requires to be frequently renewed, and thus involves much time and expense, or preferably by thin rods of moist phosphorus, which allows many hundreds of analyses to be carried out in succession. It must, however be remembered that phosphorus is not acted upon by oxygen at temperatures below 16°, consequently when the determination has to be made in a cold place, the absorption vessel must be slightly warmed in any convenient manner. Lunge recommends the use of an alkaline solution of sodium hydrosulphite, as suggested by Franzen (*cf.* p. 209), in preference to either of the above reagents for the absorption of oxygen. Since the water with the absorbents will take up any acid gases present,

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[1] *Chem. Ind.*, 1884, 7, 5.

it is necessary to wash the gas by passing it through a solution of sodium hydroxide before proceeding with the absorption of the oxygen.

When, as is usually the case, it is only necessary to make several single tests in the course of the day, the use of a special aspirator is unnecessary, as the gas burette itself suffices for this purpose by filling and emptying the burette three or four times in succession from the special opening in the gas main; it is then safe to assume that a fair sample of the gas in the main has been collected, and the analysis may be proceeded with.

The practice of making a continuous test, in addition to the above, is to be strongly recommended; that is, to draw the gas slowly during the full twenty-four hours into a special vessel, from which the sample is taken for analysis. For this purpose any suitable aspirator of wood or metal may be employed, provided the acid vapours are previously removed from the gases. The apparatus for the estimation of the acids, to be described later, effects this removal very conveniently. On the other hand, more simple appliances may be used, so long as they permit at least 10 litres of the gas to be drawn off and measured in the twenty-four hours, this quantity being essential if a representative average sample is required.

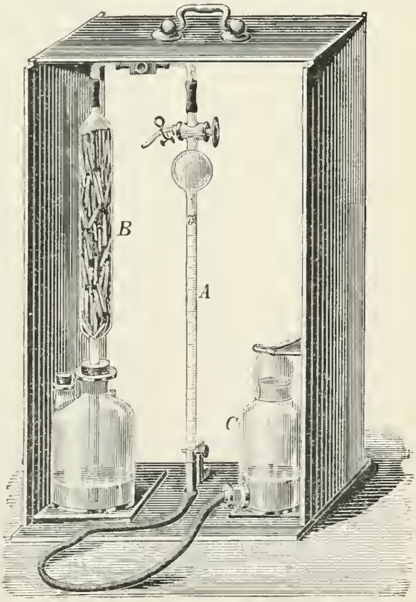

Fig. 126.

A good form of apparatus, devised by Strype for the investigation of the exit gases, is described and figured in Lunge's *Sulphuric Acid and Alkali.*[1] The apparatus described by Davis,[2] Lovett,[3] and Pringle[4] do not possess any features of special value.

The estimation of oxygen is best carried out by moist phosphorus in an Orsat apparatus (p. 198), provided with two absorption tubes, the first of which is filled with sodium hydroxide solution to remove the acid gases, and the second with phosphorus. The manipulation is exactly the same as in the examination of chimney gases (p. 198).

Lindemann's apparatus as modified by C. Winkler[5] (Fig. 126) can also be employed. The measuring tube A is fitted above with a three-way tap, and has a capacity of

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[1] Vol. i., 3rd edition, p. 739.

[2] *Chem. News*, 1880, **41**, 188.

[3] *J. Soc. Chem. Ind.*, 1882, **1**, 210.

[4] *Ibid.*, 1883, **2**, 53.

[5] *Handbook of Technical Gas Analysis*, p. 51.

100 c.c., of which 25 c.c. are contained in the lower cylindrical portion, which is graduated in $\frac{1}{10}$ c.c. B is the absorption vessel filled with thin rods of phosphorus, and C the levelling bottle. The manipulation is the same as in the Orsat apparatus.

M. Liebig's apparatus[1] is arranged for use with alkaline pyrogallol; the gas is aspirated by means of a rubber bellows into a 50 c.c. pipette, and forced from this through the absorbing solution into a graduated measuring tube.

2. **Examination for Acids.**—If only the sulphur dioxide is to be determined, a measured volume of the exit gas is drawn through sodium hydroxide solution, and the resulting solution, after considerable dilution with water, poured into chlorine or bromine water. This solution is then acidified with hydrochloric acid, heated to boiling, and precipitated with barium chloride. Each 1 g. $BaSO_4$ corresponds to 93·75 c.c. SO_2. Reich's method (p. 300) is inapplicable in this case, owing to the disturbing action exerted by the nitrous gases present.

For a complete examination the following directions will suffice. On the one hand the sum of the sulphur acids is determined, and on the other the sum of the nitrogen acids, irrespective of the degree of oxidation. The following scheme agrees in the main with that adopted by the British Alkali Makers' Association in 1878; improvements have, however, been made in some of the analytical details.

A small volume of gas is drawn continuously from the Gay-Lussac exits by means of a constant aspirator, at such a rate that at least 24 cubic feet (0·68 cub. m.) are collected in the twenty-four hours. The volume V drawn off must be measured with sufficient accuracy, either by graduating the aspirator or by means of a gas meter; the volume is then corrected by Tables VI. and VII. (Appendix) to 0° and 760 mm., and the corrected volume called V′. To make the comparisons more complete, a record is kept of the number of cubic feet of chamber space for each pound of sulphur burnt and entering the chambers in the twenty-four hours (or kilos sulphur per cubic metre), as calculated from the weekly average; further, of the distance from the tower, of the point at which the samples are taken. The gas is drawn through four absorption bottles, each of 100 c.c. capacity, and giving a column of liquid of at least 75 mm. in depth. The openings of the inlet-tubes may not exceed $\frac{1}{2}$ mm. diameter, as measured by a standard wire. The first three bottles each contain 100 c.c. of normal sodium hydroxide solution (free from nitrate and equal to 31 g. Na_2O per litre), the fourth 100 c.c. of distilled water. The gases are examined for—(1) Total acidity, measured as sulphur trioxide; (2) Sulphur; (3) Nitrogen in the form of acids, both the latter being measured in grains per cubic

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[1] Post, *Chem. Tech. Analyse*, 2nd edition, 1, p. 700.

foot, or g. per cubic metre of the gas (reduced to 0° and 760 mm.). The operation is conducted as follows:—

The contents of the four bottles are combined, the bottles washed out with a small volume of water, and the total divided into three equal parts, one portion being kept as a reserve. The first portion is titrated with normal sulphuric acid (49 g. H_2SO_4 per litre) or with normal hydrochloric acid, thus affording a measure of the total acidity, SO_2, H_2SO_4, N_2O_3, and HNO_3. The second portion is added gradually to such quantity of a warm solution of potassium permanganate, rendered strongly acid by means of pure sulphuric acid, that a slight excess of permanganate remains; this excess is finally so far neutralised by a few drops of sulphurous acid solution that only a faint rose tint persists. All the nitrogen acids are now present as nitric acid, and there is no excess of sulphurous acid in the solution. The nitric acid is estimated by means of ferrous sulphate, employing for the purpose a solution containing 100 g. crystallised ferrous sulphate, and 100 g. pure sulphuric acid per litre. To 25 c.c. of this solution contained in a flask are added a further 20 to 25 c.c. of pure concentrated sulphuric acid, and when the solution is cold the mixture resulting from the above permanganate treatment is poured in. The flask is closed by a stopper furnished with two tubes; the first is connected with a Kipp's apparatus generating carbon dioxide, the second luted in water. The air in the apparatus is expelled by the carbon dioxide, and the contents of the flask heated until the solution, which at the start is dark-coloured owing to the nitric oxide present, has become of a bright yellow colour. This may require from a quarter to one hour according to the quantity of nitric acid present, and the volume of sulphuric acid added. The ferrous salt which remains unoxidised by the nitric acid is titrated back by a $N/2$ permanganate solution equivalent to 0·004 g. oxygen per 1 c.c. (*cf.* p. 99). Since the strength of the acid ferrous sulphate solution alters somewhat rapidly, it is necessary to compare it each day with the permanganate solution by titrating 25 c.c., the quantity taken for the test, with permanganate. If x c.c. of sulphuric acid are used in the first titration, y c.c. of permanganate in titrating back the unoxidised ferrous salt, and z c.c. of permanganate are equivalent to 25 c.c. of the ferrous sulphate solution, the figures required are obtained according to the following equations; the measurement of volume (V') being of course made in cubic metres or in cubic feet according to the method of expression:—

(1) *Total acidity* expressed in—

$$\text{Grams } SO_3 \text{ per cubic metre} = \frac{0.120(100 - x)}{V'}$$

$$\text{Grains } SO_3 \text{ per cubic foot} = \frac{1.852(100 - x)}{V'}$$

(2) *Sulphur* in—

$$\text{Grams per cubic metre} = \frac{0.008(600 - 6x - z + y)}{V'}$$

$$\text{Grains per cubic foot} = \frac{0.12346(600 - 6x - z + y)}{V'}$$

(3) *Nitrogen* in—

$$\text{Grams per cubic metre} = \frac{0.007(z - y)}{V'}$$

$$\text{Grains per cubic foot} = \frac{0.10803(z - y)}{V'}$$

In place of the above method it will often suffice to simply determine the total acidity by titrating with *N*/10 sodium hydroxide solution and phenolphthalein, either according to Lunge's method, described on p. 302, or by employing the ten-bulb tube described below.

The maximum escape allowed under the Alkali Act (1906) equals 4 grains per cubic foot, equivalent to 9·15 g. SO_3 per cubic metre of residual gases, before admixture with air or smoke; in Germany the limit is 5 g. where pyrites is burnt, and 8 g. in the case of blende, all acids being calculated to SO_3.

The alkali inspectors have recently adopted a mixture of 1 vol. *N*/2 alkali and 10 vols. neutral hydrogen peroxide for the absorption of the acid gases. This overcomes the difficulty caused by secondary reactions between sulphites and nitrites which is liable to occur[1] when sodium hydroxide solution is used alone.

3. **Nitric oxide** may always be present in the exit gases even after these have passed through the absorption bottles. Should it be desired to estimate this gas, a ten-bulb absorption tube (Fig. 127) must be placed between the last flask of the series and the aspirator. The tube is filled with 30 c.c. of *N*/2 potassium permanganate solution to which 1 c.c. of sulphuric acid of sp. gr. 1·25 has been added. After the gas has passed for twenty-four hours the tube is emptied and washed out. Fifty c.c. of ferrous sulphate solution (the strength of which according to the preceeding section is = $2z$ c.c. permanganate) are added, and the decolorised solution titrated back with permanganate solution till it again becomes rose-coloured; the number of c.c. of permanganate required is called

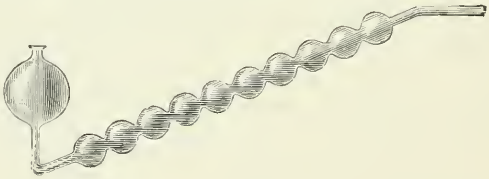

FIG. 127.

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[1] Carpenter and Linder, *J. Soc. Chem. Ind.*, 1902, **21**, 1490.

u. The nitric oxide has thus reduced $(30+u-2z)$ c.c. seminormal permanganate solution. This corresponds to:

$$N = \frac{0.007(30+u-2z)}{3V'}$$

grams nitrogen per cubic metre of the gas when V' represents the total volume, as registered by the aspirator; or in grains per cubic foot,

$$N = \frac{0.10803(30+u-2z)}{3V'}$$

A Winkler's coil, or other suitable apparatus, may be used instead of the above absorption bulbs.

To test whether all the nitric oxide has been absorbed, Griess' reagent (α-naphthylamine and sulphanilic acid), as modified by Lunge and Ilosvay,[1] may be employed, by allowing air to mix with the gases, leaving the bulb-tube and then examining for higher oxides of nitrogen. The above reagent will always show a slight reddening with such gases even where the absorption has been made as complete as possible, but for most practical purposes such traces may be neglected.

According to Divers,[2] a concentrated alkaline solution of sodium or potassium sulphite forms an excellent medium for the absorption of nitric oxide in gas analysis.

Von Knorre and Arndt[3] mix the gas with hydrogen and pass the mixture very slowly through a Drehschmidt platinum capillary tube (p. 214) heated to bright redness. If the gas be passed too quickly or the heating be insufficient, some ammonia always results. The reaction is:

$$\underset{\text{(4 vols.}}{2NO} + \underset{\text{4 vols.}}{2H_2} = 2H_2O + \underset{\text{2 vols.)}}{N_2}$$

Consequently each volume of nitric oxide corresponds to a contraction of $1\frac{1}{2}$ volumes.

Von Knorre[4] states that it is more convenient to absorb the nitric oxide in a mixture of 5 volumes of saturated potassium bichromate solution and 1 volume concentrated sulphuric acid than in the acidified permanganate solution described above, since the bichromate mixture is perfectly stable at ordinary temperatures, and does not evolve oxygen when shaken with indifferent gases; further, the nitric oxide is oxidised quantitatively to nitric acid by this mixture. A liberation of absorbed nitric oxide to indifferent gases cannot therefore occur in this case, as it may when ferrous sulphate is employed. This reagent is consequently well adapted for the removal of nitric oxide from mixtures of gases, and also for the estimation of larger amounts of this gas; for the estimation of smaller quantities such as occur in

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[1] *Z. angew. Chem.*, 1890, **3**, 568.

[2] *J. Chem. Soc.*, 1899, **75**, 82.

[3] *Ber.*, 1899, **32**, 2136.

[4] *Chem. Ind.*, 1902, **25**, 534.

the above cases, absorption in acid permanganate solution and subsequent titration is to be preferred.

4. **Nitrous oxide** in chamber or exit gases has scarcely ever been estimated up to the present. The earlier known method of Winkler,[1] which consists in the removal of the nitrogen acids and oxygen from the gases and conversion of the nitrogen compounds in the residue into ammonia by passing them together with excess of hydrogen over gently heated palladium asbestos, and that of Lunge,[2] which is carried out by first acting upon the gases with concentrated potassium hydroxide solution and permanganate, shaking the residue with absolute alcohol, and decomposing the gases expelled from the latter into nitrogen and oxygen by means of a glowing palladium wire, do not suffice where the quantity of nitrous oxide present is so small and is admixed with a largely preponderating amount of nitrogen. The process worked out by Pollak[3] is preferable. The mixture of NO, N_2O, and N, from which all oxygen has previously been removed by means of moist phosphorus, is burnt either with hydrogen or with carbonic oxide in a Drehschmidt tube. The contraction, V_c, is noted, oxygen added to the residual gas, and the mixture again burnt in the capillary. Two-thirds of the resulting contraction is equal to the volume of hydrogen that remains after the first combustion, and this subtracted from the volume of hydrogen originally added gives the volume of hydrogen used, V_w. We thus have :—

$$(1)\ xN_2O + yNO + zN = V$$
$$(2)\ x + 3/2y = V_c$$
$$(3)\ x + y = V_w$$

from which :—

$$x = 3V_w - 2V_c$$
$$y = 2(V_c - V_w)$$
$$z = V - V_w$$

In the case of combustion with carbon monoxide the contraction, V_c, and the carbon dioxide formed, V_k, are measured.

This gives :—

$$(1)\ xN_2O + yNO + zN = V$$
$$(2)\ 1/2y = V_c$$
$$(3)\ x + y = V_k$$

from which it follows :—

$$x = V_k - 2V_c$$
$$y = 2V_c$$
$$z = V - V_k$$

For the proof of these formulæ, see Treadwell, *loc. cit.*

5. **Loss of Sulphur.**—Lunge[4] has published a formula which allows

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[1] *Industrie-Gase*, vol. 2, p. 429.

[2] *Ber.*, 1881, 14, 2188.

[3] Treadwell, *Analytical Chemistry*, vol. ii., p. 612.

[4] Cf. *Sulphuric Acid and Alkali*, vol. i., p. 749; *Dingl. polyt. J.*, 1877, 226, 634.

the quantity of sulphur burnt, expressed in grams per litre on the exit gases, to be calculated from the percentage volume of oxygen present in these. The sulphur loss may be calculated by comparing this value with the quantity of sulphur acids present in the exit gases. The formula is:

$$x = (20.95 - a)0.009637 \frac{1}{1.00367t} \frac{h}{760}$$

where x equals the total sulphur burnt, expressed in grams per litre on the exit gas, a the percentage volume of oxygen in the exit gas, t its temperature, and h the pressure.

Examination of the Works' Acids

The strength of the *Drips* from the chambers is observed at frequent intervals during the day and their content in nitrous vitriol gauged, at least by a rough test. The latter can, of course, be more exactly estimated by means of permanganate solution. Tests of the bottom-acid are also made.

For collecting the "drips" Lunge[1] recommends the use of small cylinders of 20 c.c. capacity and correspondingly small hydrometers having a range of about 20° Tw., in place of the customary larger cylinder and full-range hydrometers. The smaller cylinders have the advantage that the acid is renewed about every ten minutes, and thus show any changes more quickly.

For a rapid, approximate determination of the *Nitrosity* (percentage of nitrogen acids) of the drips, Lunge[2] recommends the following method for testing a set of four chambers. The test should be performed at least once, better twice, daily, and for each test a stand furnished with eight ordinary test tubes, each 13 cm. high, is employed. The test tubes are each filled to a height of 10 cm. with samples of the bottom-acid and of the drip-acid respectively, of each of the chambers, taken in turn. The strength of each sample is taken at the same time by the hydrometer and written on the stand at the bottom of the respective tube. Concentrated ferrous sulphate solution, which does not require to be free from ferric salts, is then cautiously added so as to form a layer about 1 cm. deep on the acid in each cylinder. In the presence of very minute traces of nitric acid or of the lower oxides of nitrogen a yellowish coloured ring results at the junction of the liquids. In the presence of larger amounts of nitrogen acids the ring is darker, or with still greater quantities the whole of the ferrous sulphate layer assumes a deep brown to black colour, and may even begin to froth owing to the heat evolved driving off the dissolved nitric oxide from the solution. By an inspection of the various colours in their sequence from chamber to chamber, coupled with the strength of the acid from each chamber and

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[1] *Sulphuric Acid and Alkali*, vol. i., p. 507.

[2] *Ibid.*, p. 699.

the colour of the gases in the latter, a very good indication of the operation of the chamber process is obtained. The estimation of the sulphur dioxide in the inlet gases and of the oxygen in the exit gases complete the necessary testing.

The bottom-acid in the first chamber should show no trace of nitrous acid. In the middle chambers the test should indicate a small quantity of nitrous acid in the bottom-acid and a more pronounced quantity in the drips. The bottom-acid in the last chamber should give at least a moderate indication, and the drips a very marked reaction.

Should selenium be present the ferrous sulphate test is not so easily applied; it may, however, be successfully employed after some practice.

For the quantitative estimation of the nitrogen acids in vitriol the potassium bichromate method was formerly generally employed, but it has now been replaced by the permanganate method, which gives a much sharper end-reaction. The details of the permanganate method are given under "Gay-Lussac acid" (p. 343).

It has been suggested that the daily production of acid might be deduced by measuring the drips from the chambers. Lunge[1] has shown, however, that this view is incorrect, owing to the drip tables acting as contact surfaces. They consequently not only collect the acid normally produced at the point of the chamber considered, but also the much larger volume of acid condensed locally either by mechanical means or owing to a better admixture of, and accompanying reaction in, the chamber gases impinging against the solid wall.

The yield of chamber acid should be determined directly by measuring the acid dip in the chambers, which is done by means of vessels communicating with the interior. It is advisable to draw up a table for each chamber, so as to see at a glance the volume of acid, in cubic feet or litres, corresponding to any observed dip. If the specific gravity be determined at the same time by means of the hydrometer, the weight of acid in the chamber can be calculated.

Examination of the Glover acid. The strength (140° to 150° Tw., sp. gr. 1·7 to 1·75) and temperature are determined in case the acid is to be pumped back at once to the Gay-Lussac tower; also the content in nitrous compounds, should more than traces of these be present. (This determination is described in connection with the finished acid, p. 377.) Other tests are carried out exactly as in the case of the nitrous vitriol from the Gay-Lussac tower.

Examination of the Gay-Lussac acid (*Nitrous vitriol*). Generally only the nitrous acid is determined; this is not present in the vitriol in the free condition, but is combined to form nitrosyl-sulphuric acid $SO_2(OH)(ONO)$. Nitric acid only occurs in poor nitrous vitriol; it is included in the total nitrogen found by the nitrometer test.

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[1] *Z. angew. Chem.*, 1889, **2**, 265.

Nitrous acid is usually estimated by the permanganate method; the bichromate method is to-day seldom employed (cf. *supra*). The test is carried out in the manner proposed by Lunge,[1] who has shown that the earlier methods employed were inaccurate, owing to the ready loss of nitric oxide and production of nitric acid that took place before the reaction with permanganate was effected. A seminormal permanganate solution, prepared and standardised as described (p. 99), is employed. The essential point to be observed is that the nitrous vitriol must always be added to the permanganate, and never the reverse. The test is carried out by allowing the sample to flow from a glass-tap burette into a measured volume of the $N/2$ permanganate solution, diluted with five times its volume of warm water (30° to 40°), until the colour just vanishes. At the ordinary temperature the reaction proceeds too slowly, whilst at too high a temperature or in too concentrated solution hydrated manganese dioxide separates out; such separation gives trouble, but it does not prevent the titration being carried to a finish, since the dioxide goes into solution again before the completion of the titration. The quantity of permanganate taken varies according as the vitriol to be tested contains much or little nitrous acid; 1 c.c. permanganate corresponds to 0·009502 g. N_2O_3. For chamber acid or other similar acid, 5 c.c. of permanganate solution at most are taken; for a strong nitrous vitriol up to 50 c.c. If the volume of permanganate solution taken be denoted by x, and the volume of nitrous vitriol required to decolorise it by y, the weight of N_2O_3 in g. per litre is given by the formula $\frac{9{\cdot}502x}{y}$. Should it be desired to express the nitrogen content otherwise than as N_2O_3, the factor 9·502 is substituted by 15·75 for HNO_3, by 29·83 for nitric acid of 66°·5 Tw. at 15° C., by 25·44 for nitric acid of 77° Tw., and by 21·258 for $NaNO_3$.

The following table (p. 344) saves calculation for cases in which 50 c.c. of permanganate solution are employed. The number of c.c. of nitrous vitriol required are given in column y, the content in g. per litre in column a, and in column b the percentage by weight, assuming the acid examined to be of sp. gr. 1·7 (140° Tw.). For other strengths of acid the percentage by weight is found by dividing the values in column a by ten times the specific gravity of the acid.

Riegler[2] has proposed to estimate the nitrous acid by the gas-volumetric method, using hydrogen peroxide according to the reaction:—

$$HNO_2 + H_2O_2 = H_2O + HNO_3.$$

Grützner[3] estimates the nitrite by determining the chloride produced by interaction with chloric acid by Volhard's method (p. 123):—

$$3HNO_2 + HClO_3 = 3HNO_3 + HCl.$$

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[1] *Ber.*, 1877, **10**, 1075.

[2] *Z. anal. Chem.*, 1897, **36**, 665.

[3] *Arch. Pharm.*, **35**, 241.

Table for the estimation of Nitrous Acid in Nitrous Vitriol.

Expressed as HNO_3, $NaNO_3$, and as nitric acid of 66°·5 and 77° Tw. at 15° C., in which 50 c.c. *N*/2 potassium permanganate is taken for the titration, and the percentages by weight are based on sulphuric acid of 140° Tw. as unit.

Acid required.	HNO_3.		$NaNO_3$.		Nitric Acid 66°·5 Tw.		Nitric Acid 77° Tw.	
y. c.c.	*a*. G. per Litre.	*b*. Percentage by Weight.	*a*. G. per Litre.	*b*. Percentage by Weight.	*a*. G. per Litre.	*b*. Percentage by Weight.	*a*. G. per Litre.	*b*. Percentage by Weight.
10	78·8	4·61	106·3	6·22	149·1	8·72	127·2	7·44
11	71·6	4·19	96·6	5·65	135·6	7·93	115·6	6·76
12	65·6	3·84	88·6	5·18	124·3	7·27	106·0	6·20
13	60·6	3·54	81·8	4·78	114·7	6·70	97·8	5·72
14	56·2	3·29	75·9	4·44	106·5	6·23	90·8	5·31
15	52·5	3·07	70·9	4·14	99·4	5·80	84·8	4·96
16	49·2	2·88	66·4	3·88	93·2	5·45	79·5	4·65
17	46·3	2·71	62·5	3·65	87·7	5·13	74·8	4·37
18	43·7	2·56	59·0	3·45	82·9	4·85	70·7	4·13
19	41·5	2·42	55·9	3·27	78·5	4·59	66·9	3·91
20	39·4	2·30	53·1	3·11	74·6	4·36	63·6	3·72
21	37·5	2·19	50·6	2·96	71·0	4·15	60·6	3·54
22	35·8	2·09	48·3	2·82	67·8	3·96	57·8	3·38
23	34·2	2·00	46·2	2·70	64·8	3·79	55·3	3·23
24	32·8	1·92	44·3	2·60	62·1	3·62	53·0	3·11
25	31·5	1·84	42·5	2·49	59·7	3·49	50·8	2·97
26	30·3	1·77	40·9	2·39	57·4	3·35	48·9	2·86
27	29·2	1·71	39·4	2·30	55·2	3·25	47·1	2·75
28	28·1	1·65	38·0	2·22	53·3	3·12	45·4	2·66
29	27·1	1·59	36·7	2·15	51·4	3·01	43·9	2·56
30	26·3	1·54	35·4	2·07	49·7	2·91	42·4	2·48
31	25·4	1·49	34·3	2·01	48·1	2·81	41·0	2·40
32	24·6	1·44	33·2	1·94	46·6	2·73	39·7	2·32
33	23·9	1·40	32·2	1·88	45·2	2·64	38·5	2·25
34	23·2	1·35	31·3	1·84	43·9	2·56	37·4	2·19
35	22·5	1·32	30·4	1·78	42·6	2·49	36·3	2·13
36	21·9	1·28	29·5	1·73	41·4	2·42	35·3	2·07
37	21·3	1·24	28·7	1·68	40·3	2·36	34·4	2·01
38	20·7	1·21	28·0	1·64	39·3	2·30	33·5	1·96
39	20·2	1·18	27·3	1·60	38·2	2·23	32·6	1·91
40	19·7	1·15	26·5	1·55	37·3	2·18	31·8	1·86
41	19·2	1·12	25·8	1·51	36·4	2·13	31·0	1·81
42	18·8	1·10	25·3	1·48	35·5	2·08	30·3	1·77
43	18·3	1·07	24·7	1·45	34·6	2·02	29·5	1·73
44	17·9	1·05	24·2	1·42	33·9	1·98	28·9	1·69
45	17·5	1·02	23·6	1·38	33·1	1·93	28·2	1·65
46	17·1	1·00	23·1	1·35	32·4	1·90	27·6	1·62
47	16·7	0·98	22·6	1·32	31·7	1·85	27·0	1·58
48	16·4	0·96	22·2	1·30	31·1	1·82	26·5	1·55
49	16·1	0·94	21·7	1·27	30·4	1·78	25·9	1·51
50	15·8	0·921	21·3	1·25	29·8	1·74	25·4	1·49
55	14·3	0·837	19·3	1·13	27·1	1·59	23·1	1·35
60	13·1	0·768	17·7	1·04	24·5	1·45	21·2	1·24
65	12·1	0·709	16·4	0·96	22·9	1·34	19·6	1·14
70	11·2	0·658	15·2	0·89	21·3	1·25	18·2	1·06
75	10·5	0·614	14·17	0·829	19·9	1·16	16·96	0·99
80	9·85	0·576	13·3	0·778	18·6	1·09	15·9	0·93
85	9·2	0·542	12·5	0·731	17·5	1·03	14·9	0·87
90	8·7	0·511	11·8	0·692	16·5	0·967	14·1	0·825
95	8·3	0·485	11·2	0·655	15·7	0·918	13·4	0·783
100	7·9	0·461	10·6	0·620	14·9	0·873	12·7	0·744

The estimation of the total nitrogen acids present in nitrous vitriol is generally effected in the nitrometer, the use of which for this purpose has been already described (p. 134). Should the acid contain, in addition to the nitrous acid, appreciable quantities of sulphur dioxide, which can readily be detected by the smell, a little powdered potassium permanganate is placed in the cup of the nitrometer; a large excess of permanganate must not be used, since it interferes considerably with the reaction.

The observed gas volume must be reduced to 0° and 760 mm. by means of the Tables VI. and VII. (Appendix), unless the gas-volumeter (*cf.* p. 138) be employed; with the latter instrument it is especially advisable to use a separate decomposition vessel.

The nitrogen compounds are calculated from the corrected nitric oxide volumes by means of the following table. The table takes account of the various ways of stating results adopted in different works, and will be found useful in other than sulphuric acid works. Column *a* gives the values in milligrams throughout, column *b* the percentage by weight, assuming that 1 c.c. of acid of 142° Tw. has been taken for analysis; for other strengths of acid the values under *a* must be taken as the basis for calculation (*cf.* p. 343).

c.c. NO.	N.		NO.		N_2O_3.	
	a. mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.
1	0·6257	0·0366	1·3402	0·0784	1·6975	0·0993
2	1·2514	0·0732	2·6804	0·1568	3·3950	0·1986
3	1·8771	0·1098	4·0206	0·2352	5·0925	0·2979
4	2·5028	0·1464	5·3608	0·3136	6·7900	0·3972
5	3·1385	0·1830	6·7010	0·3920	8·4875	0·4965
6	3·7542	0·2196	8·0412	0·4704	10·1850	0·5958
7	4·3799	0·2562	9·3814	0·5488	11·8825	0·6951
8	5·0056	0·2928	10·7216	0·6272	13·5800	0·7944
9	5·6313	0·3294	12·0618	0·7056	15·2775	0·8937

c.c. NO.	HNO_3.		Nitric Acid 66°·5 Tw.		$NaNO_3$.	
	a. mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.
1	2·8144	0·1646	5·333	0·312	3·7986	0·2221
2	5·6288	0·3292	10·666	0·624	7·5972	0·4442
3	8·4432	0·4938	15·999	0·936	11·3958	0·6663
4	11·2576	0·6584	21·332	1·248	15·1944	0·8884
5	14·0720	0·8230	26·665	1·560	18·9930	1·1105
6	16·8864	0·9876	31·998	1·872	22·7916	1·3326
7	19·7008	1·1522	37·331	2·184	26·5902	1·5547
8	22·5152	1·3168	42·664	2·496	30·3888	1·7768
9	25·3296	1·4814	47·997	2·808	34·1874	1·9989

One hundred parts of nitric acid of 66°·5 Tw. correspond to 71·23 parts pure $NaNO_3$, or 74·20 parts of 96 per cent. Chili saltpetre.

Ratio of the three nitrogen acids to each other. The following formulæ may be used to determine the relationship between the N_2O_3, N_2O_4, and HNO_3, present together in sulphuric acid when the results of the permanganate titration and the nitrometer determination of total nitrogen in the form of NO are known:—

a = c.c. NO, as found in the nitrometer;
b = c.c. O, calculated from the permanganate titration (1 c.c. O = 1·4278 mg., consequently 1 c.c. $N/2$ permanganate = 0·004 g. = 2·8015 c.c. oxygen);
x = vol. NO, corresponding to N present as N_2O_3;
y = vol. NO, ” ” N_2O_4;
z = vol. NO, ” ” HNO_3.

If $4b > a$, then:—

$$x = 4b - a;\ y = 2(a - 2b) \text{ or } = a - x.$$

If $4b < a$, then:—

$$y = 4b;\ z = a - 4b.$$

That is, if the oxygen is sufficient to allow of all the nitrogen acids being present as N_2O_4, they are calculated as such; if there is more than sufficient oxygen for this the excess is calculated to HNO_3, whilst if there is less oxygen the deficit is calculated to N_2O_3. In practice, the ordinary nitrous vitriol contains no N_2O_4, on which account it is better to calculate the total oxygen deficit (as determined by permanganate) to N_2O_3 or to nitrosyl-sulphuric acid, the rest of the nitrogen being calculated to nitric acid.

FINISHED PRODUCT: SULPHURIC ACID

Sulphuric acid appears in commerce as chamber acid of 106° to 116° Tw.; as 140° Tw. acid from the Glover tower, or after evaporation in lead pans; as ordinary 168° Tw. acid (93 to 95 per cent.); as extra concentrated acid (96 to 98 per cent.); as commercial monohydrate, and as fuming sulphuric acid. The last will be dealt with separately.

Actual sulphuric acid, generally referred to as monohydrate, H_2SO_4, has a specific gravity of 1·853 at 0° and, according to different observers, of 1·8372 to 1·8384 at 15° compared with water at 4°. The German Standards Commission calculate the specific gravity of actual monohydrate as 1·8357 at 15°/4° by extrapolation; it should, however, be borne in mind in connection with this extraordinarily low value, that owing to the remarkable irregularities that occur in the density curve when such high concentrations are reached extrapolation may be very misleading. The maximum specific gravity (1·8415) lies between 97 and 98 per cent. acid, and the density of the monohydrate is thus increased by addition of a little water as well as by addition of sulphuric anhydride. The monohydrate begins to boil at 290°, and at first evolves some SO_3, the boiling point rising to 338°, at which temperature 98 per cent of H_2SO_4 and 2 per cent. of H_2O are present.[1]

The strength of sulphuric acid is generally determined by its specific gravity. The earlier tables in use have been found to be altogether unreliable, especially at the higher concentrations, and Lunge and Isler[2] consequently worked out a new table based on fresh observations, using, however, the values previously determined by Lunge and Naef[3] for acids of over 90 per cent. H_2SO_4. All uncertainty in this connection has now been removed by the very exhaustive and painstaking investigations of Domke, Bein, Fischer and others, whose work is embodied in the reports of the German Standards Commission.[4] This work, undertaken in the first place in connection with the establishment of the normals for percentage hydrometers, has been carried out with such care that the results may safely be looked upon as exact; the report contains in addition a detailed description and criticism of all previous work on the subject.

The following tables are taken from this source. (1) The table for the estimation of the sp. gr. of pure sulphuric acid-water mixtures from the percentage content for 15° C./4° C.; the fifth decimal place, which was only determined for purposes of calculation, is omitted, but has been used to round off the fourth figure. (2) An extract from the tables for reducing to 15° C. the reading found at some other temperature. The original memoir contains many other tables of less importance for the present purpose, and which are not included here.

In these tables the values are given for progressively increasing percentages of sulphuric acid. The form adopted in the tables prepared by Lunge, based upon measurements made in conjunction with Isler and Naef, is much more useful for works and laboratory purposes. These tables are accordingly included; they have been recalculated to the values of the German Standards Commission for all cases in which they differed by more than 0·1 per cent. Larger variations than this scarcely appear below the specific gravity of 1·560 but between this point and 1·680 differences rising up to about ¾ per cent. occur; the causes of these divergencies have not been discovered up to the present. Still greater differences exist at certain of the higher concentrations, especially from 96 per cent. onwards, but at these strengths the determination of the acid content by means of the specific gravity is quite unreliable, and consequently the readings do not come into question for practical purposes. Perhaps the most pronounced variation (0·54 per cent.) occurs at 99½ per cent., and it is interesting to note that Koechlin and Gerber have shown that at this extremely high concentration acids prepared in different ways may, although of the same

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. 1, p. 173.

[2] *Z. angew. Chem.*, 1890, **3**, 131.

[3] *Chem. Ind.*, 1883, **6**, 37.

[4] *Abhandlungen*, 1904, vol. **5**.

chemical composition, possess different physical properties, a view hinted at by Lunge in 1883. A greater degree of accuracy than 0·1 per cent. is not likely to be attained in practice, and this limit is more than sufficient for the tables, since the figures given are for chemically pure acid which is not found in ordinary practical work. It may be noted that the German Standards Commission always worked to temperatures as recorded by the hydrogen scale, which at 15° gives values 0·1 lower than those recorded on the mercury scale.

Table for determining the Specific Gravity of Pure Sulphuric Acid-water Mixtures from the Percentage Content.

Per cent. Sulphuric Acid.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
	Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.									
0	0·9991	0·9998	1·0005	1·0012	1·0019	1·0026	1·0033	1·0040	1·0047	1·0054
1	1·0061	1·0068	1·0079	1·0082	1·0088	1·0095	1·0102	1·0109	1·0116	1·0122
2	1·0129	1·0136	1·0143	1·0149	1·0156	1·0163	1·0170	1·0176	1·0183	1·0190
3	1·0197	1·0203	1·0210	1·0217	1·0224	1·0230	1·0237	1·0244	1·0251	1·0257
4	1·0264	1·0271	1·0277	1·0284	1·0291	1·0298	1·0304	1·0311	1·0318	1·0325
5	1·0332	1 0338	1·0345	1·0352	1·0359	1·0366	1·0373	1·0380	1·0386	1·0393
6	1·0400	1·0407	1·0414	1·0421	1·0428	1·0435	1·0442	1·0449	1·0456	1·0462
7	1·0469	1·0476	1·0483	1·0490	1·0497	1·0504	1·0511	1·0518	1·0525	1·0532
8	1·0539	1·0546	1·0554	1·0561	1·0568	1·0575	1·0582	1·0589	1·0596	1·0603
9	1·0610	1·0617	1·0624	1·0631	1·0638	1·0645	1·0653	1·0660	1·0667	1·0674
10	1·0681	1·0688	1·0695	1·0702	1·0710	1·0717	1·0724	1·0731	1·0738	1·0745
11	1·0753	1·0760	1·0767	1·0774	1·0781	1·0789	1·0796	1·0803	1·0810	1·0818
12	1·0825	1·0832	1·0839	1·0847	1·0854	1·0861	1·0868	1·0876	1·0883	1·0890
13	1·0898	1·0905	1·0912	1·0920	1·0927	1·0934	1·0942	1·0949	1·0956	1·0964
14	1·0971	1·0978	1·0986	1·0993	1·1000	1·1008	1·1015	1·1023	1·1030	1·1038
15	1·1045	1·1052	1·1060	1·1067	1·1075	1·1082	1·1090	1·1097	1·1105	1·1112
16	1·1120	1·1127	1·1135	1·1142	1·1150	1·1157	1·1165	1·1172	1·1180	1·1187
17	1·1195	1·1202	1·1210	1·1217	1·1225	1·1233	1·1240	1·1248	1·1255	1·1263
18	1·1270	1·1278	1·1286	1·1293	1·1301	1·1309	1·1316	1·1324	1·1331	1·1339
19	1·1347	1·1354	1·1362	1·1370	1·1377	1·1385	1·1393	1·1400	1·1408	1·1416
20	1·1424	1·1431	1·1439	1·1447	1·1454	1·1462	1·1470	1·1478	1·1485	1·1493
21	1·1501	1·1509	1·1516	1·1524	1·1532	1·1540	1·1548	1·1555	1·1563	1·1571
22	1·1579	1·1587	1·1594	1·1602	1·1610	1·1618	1·1626	1·1634	1·1641	1·1649
23	1·1657	1·1665	1·1673	1·1681	1·1689	1·1697	1·1705	1·1712	1·1720	1·1728
24	1·1736	1·1744	1·1752	1·1760	1·1768	1·1776	1·1784	1·1792	1·1800	1·1808
25	1·1816	1·1824	1·1832	1·1840	1·1848	1·1856	1·1864	1·1872	1·1880	1·1888
26	1·1896	1·1904	1·1912	1·1920	1·1928	1·1936	1·1944	1·1952	1·1960	1·1968
27	1·1976	1·1984	1·1992	1·2000	1·2008	1·2016	1·2025	1·2033	1·2041	1·2049
28	1·2057	1·2065	1·2073	1·2081	1·2089	1·2098	1·2106	1·2114	1·2122	1·2130
29	1·2138	1·2146	1·2155	1·2163	1·2171	1·2179	1·2187	1·2196	1·2204	1·2212
30	1·2220	1·2228	1·2237	1·2245	1·2253	1·2261	1·2270	1·2278	1·2286	1·2294
31	1·2302	1·2311	1·2319	1·2327	1·2335	1·2344	1·2352	1·2360	1·2368	1·2377
32	1·2385	1·2393	1·2402	1·2410	1·2418	1·2426	1·2435	1·2443	1·2451	1·2460
33	1·2468	1·2476	1·2485	1·2493	1·2501	1·2510	1·2518	1·2526	1·2535	1·2543
34	1·2552	1·2560	1·2568	1·2577	1·2585	1·2594	1·2602	1·2610	1·2619	1·2627

Specific Gravity of Pure Sulphuric Acid-water—*Continued.*

Per cent. Sulphuric Acid.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
	Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.									
35	1·2636	1·2644	1·2653	1·2661	2·2670	1·2678	1·2686	1·2695	1·2703	1·2712
36	1·2720	1·2729	1·2737	1·2746	1·2754	1·2763	1·2771	1·2780	1·2788	1·2797
37	1·2806	1·2814	1·2823	1·2831	1·2840	1·2848	1·2857	1·2866	1·2874	1·2883
38	1·2891	1·2900	1·2909	1·2917	1·2926	1·2935	1·2943	1·2952	1·2961	1·2969
39	1·2978	1·2987	1·2995	1·3004	1·3013	1·3022	1·3030	1·3039	1·3048	1·3057
40	1·3065	1·3074	1·3083	1·3092	1·3101	1·3109	1·3118	1·3127	1·3136	1·3145
41	1·3153	1·3162	1·3171	1·3180	1·3189	1·3198	1·3207	1·3215	1·3224	1·3233
42	1·3242	1·3251	1·3260	1·3269	1·3278	1·3287	1·3296	1·3305	1·3314	1·3323
43	1·3332	1·3341	1·3350	1·3359	1·3368	1·3377	1·3386	1·3395	1·3404	1·3413
44	1·3423	1·3432	1·3441	1·3450	1·3459	1·3468	1·3478	1·3487	1·3496	1·3505
45	1·3514	1·3524	1·3533	1·3542	1·3551	1·3561	1·3570	1·3579	1·3589	1·3598
46	1·3607	1·3617	1·3626	1·3635	1·3645	1·3654	1·3664	1·3673	1·3682	1·3692
47	1·3701	1·3711	1·3720	1·3730	1·3739	1·3749	1·3758	1·3768	1·3777	1·3787
48	1·3796	1·3806	1·3816	1·3825	1·3835	1·3844	1·3854	1·3864	1·3873	1·3883
49	1·3893	1·3902	1·3912	1·3922	1·3931	1·3941	1·3951	1·3961	1·3970	1·3980
50	1·3990	1·4000	1·4010	1·4019	1·4029	1·4039	1·4049	1·4059	1·4069	1·4079
51	1·4088	1·4098	1·4108	1·4118	1·4128	1·4138	1·4148	1·4158	1·4168	1·4178
52	1·4188	1·4198	4·4208	1·4218	1·4228	1·4238	1·4249	1·4259	1·4269	1·4279
53	1·4289	1·4299	1·4309	1·4319	1·4330	1·4340	1·4350	1·4360	1·4370	1·4381
54	1·4391	1·4401	1·4411	1·4422	1·4432	1·4442	1·4453	1·4463	1·4473	1·4484
55	1·4494	1·4504	1·4515	1·4525	1·4535	1·4546	1·4556	1·4567	1·4577	1·4587
56	1·4598	1·4608	1·4619	1·4629	1·4640	1·4650	1·4661	1·4671	1·4682	1·4692
57	1·4703	1·4714	1·4724	1·4735	1·4745	1·4756	1·4767	1·4777	1·4788	1·4798
58	1·4809	1·4820	1·4837	1·4841	1·4852	1·4863	1·4873	1·4884	1·4895	1·4905
59	1·4916	1·4927	1·4938	1·4949	1·4960	1·4970	1·4981	1·4992	1·5003	1·5013
60	1·5024	1·5035	1·5046	1·5057	1·5068	1·5079	1·5090	1·5101	1·5112	1·5122
61	1·5133	1·5144	1·5155	1·5166	1·5177	1·5188	1·5199	1·5210	1·5221	1·5232
62	1·5243	1·5254	1·5265	1·5276	1·5287	1·5298	1·5309	1·5321	1·5332	1·5343
63	1·5354	1·5365	1·5376	1·5387	1·5398	1·5410	1·5421	1·5432	1·5443	1·5454
64	1·5465	1·5477	1·5488	1·5499	1·5510	1·5521	1·5533	1·5544	1·5555	1·5566
65	1·5578	1·5589	1·5600	1·5612	1·5623	1·5634	1·5645	1·5657	1·5668	1·5679
66	1·5691	1·5702	1·5713	1·5725	1·5736	1·5748	1·5759	1·5770	1·5782	1·5793
67	1·5805	1·5816	1·5827	1·5839	1·5850	1·5862	1·5873	1·5885	1·5896	1·5908
68	1·5919	1·5931	1·5942	1·5954	1·5965	1·5977	1·5989	1·6000	1·6012	1·6023
69	1·6035	1·6046	1·6058	1·6070	1·6081	1·6093	1·6104	1·6116	1·6128	1·6139
70	1·6151	1·6163	1·6174	1·6186	1·6198	1·6209	1·6221	1·6233	1·6245	1·6256
71	1·6268	1·6280	1·6291	1·6303	1·6315	1·6327	1·6338	1·6350	1·6362	1·6374
72	1·6385	1·6397	1·6409	1·6421	1·6433	1·6444	1·6456	1·6468	1·6480	1·6492
73	1·6503	1·6515	1·6527	1·6539	1·6551	1·6563	1·6574	1·6586	1·6598	1·6610
74	1·6622	1·6634	1·6645	1·6657	1·6669	1·6681	1·6693	1·6705	1·6717	1·6728
75	1·6740	1·6752	1·6764	1·6776	1·6788	1·6799	1·6811	1·6823	1·6835	1·6847
76	1·6858	1·6870	1·6882	1·6894	1·6906	1·6917	1·6929	1·6941	1·6953	1·6965
77	1·6976	1·6988	1·7000	1·7012	1·7023	1·7035	1·7047	1·7058	1·7070	1·7082
78	1·7093	1·7105	1·7117	1·7128	1·7140	1·7151	1·7163	1·7175	1·7186	1·7198
79	1·7209	1·7221	1·7232	1·7244	1·7255	1·7267	1·7278	1·7289	1·7301	1·7312

Specific Gravity of Pure Sulphuric Acid-water—*Continued.*

Per cent. Sulphuric Acid.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
	Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.									
80	1·7324	1·7335	1·7346	1·7357	1·7369	1·7380	1·7391	1·7402	1·7413	1·7424
81	1·7435	1·7446	1·7457	1·7468	1·7479	1·7490	1·7501	1·7512	1·7523	1·7534
82	1·7544	1·7555	1·7566	1·7576	1·7587	1·7597	1·7608	1·7618	1·7628	1·7639
83	1·7649	1·7659	1·7669	1·7679	1·7689	1·7699	1·7709	1·7719	1·7729	1·7738
84	1·7748	1·7758	1·7767	1·7777	1·7786	1·7796	1·7805	1·7814	1·7823	1·7832
85	1·7841	1·7850	1·7859	1·7868	1·7876	1·7885	1·7894	1·7902	1·7911	1·7919
86	1·7927	1·7935	1·7943	1·7951	1·7959	1·7967	1·7975	1·7983	1·7991	1·7998
87	1·8006	1·8013	1·8021	1·8028	1·8035	1·8042	1·8049	1·8056	1·8063	1·8070
88	1·8077	1·8084	1·8090	1·8097	1·8103	1·8110	1·8116	1·8122	1·8129	1·8135
89	1·8141	1·8147	1·8153	1·8158	1·8164	1·8170	1·8176	1·8181	1·8187	1·8192
90	1·8198	1·8203	1·8208	1·8213	1·8219	1·8224	1·8229	1·8234	1·8239	1·8244
91	1·8248	1·8253	1·8258	1·8262	1·8267	1·8271	1·8276	1·8280	1·8284	1·8289
92	1·8293	1·8297	1·8301	1·8305	1·8309	1·8313	1·8317	1·8320	1·8324	1·8328
93	1·8331	1·8335	1·8338	1·8341	1·8345	1·8348	1·8351	1·8354	1·8357	1·8360
94	1·8363	1·8366	1·8369	1·8371	1·8374	1·8376	1·8379	1·8381	1·8384	1·8386
95	1·8388	1·8390	1·8392	1·8394	1·8396	1·8398	1·8400	1·8401	1·8403	1·8404
96	1·8406	1·8407	1·8408	1·8409	1·8410	1·8411	1·8412	1·8413	1·8414	1·8414
97	1·8414	1·8415	1·8415	1·8415	1·8415	1·8415	1·8414	1·8414	1·8413	1·8412
98	1·8411	1·8410	1·8409	1·8408	1·8406	1·8405	1·8403	1·8401	1·8398	1·8396
99	1·8393	1·8391	1·8388	1·8385	1·8381	1·8378	(1·8374)	(1·8370)	(1·8366)	(1·8362)
100	(1·8357)	...	...	...	...	...	...	...	...	...

(The bracketed values from 99·6 to 100 per cent. are extrapolated.)

Specific Gravity of Sulphuric Acid Solutions.
Lunge, Isler, and Naef.

Sp. Gr. at $\frac{15^\circ}{4^\circ}$ (*in vacuo.*)	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4,	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·000	0	0	0·07	0·09	0·12	0·14	0·001	0·001	0·001	0·001
1·005	0·7	1	0·77	0·95	1·21	1·52	0·008	0·009	0·013	0·015
1·010	1·4	2	1·28	1·57	2·01	2·51	0·013	0·016	0·020	0·025
1·015	2·1	3	1·88	2·30	2·95	3·68	0·019	0·023	0·030	0·037
1·020	2·7	4	2·47	3·03	3·88	4·85	0·025	0·031	0·040	0·050
1·025	3·4	5	3·07	3·76	4·82	6·02	0·032	0·039	0·049	0·062
1·030	4·1	6	3·67	4·49	5·78	7·18	0·038	0·046	0·059	0·074
1·035	4·7	7	4·27	5·23	6·73	8·37	0·044	0·054	0·070	0·087
1·040	5·4	8	4·87	5·96	7·64	9·54	0·051	0·062	0·079	0·099
1·045	6·0	9	5·45	6·67	8·55	10·67	0·057	0·071	0·089	0·112
1·050	6·7	10	6·02	7·37	9·44	11·79	0·063	0·077	0·099	0·124
1·055	7·4	11	6·59	8·07	10·34	12·91	0·070	0·085	0·109	0·136
1·060	8·0	12	7·16	8·77	11·24	14·03	0·076	0·093	0·119	0·149
1·065	8·7	13	7·73	9·47	12·14	15·15	0·082	0·102	0·129	0·161
1·070	9·4	14	8·32	10·19	13·05	16·30	0·089	0·109	0·140	0·174
1·075	10·0	15	8·90	10·90	13·96	17·44	0·096	0·117	0·150	0·188

Specific Gravity of Sulphuric Acid Solutions—*Continued.*

Sp. Gr. at $\frac{15^\circ}{4^\circ}$ *(in vacuo.)*	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·080	10·6	16	9·47	11·60	14·87	18·56	0·103	0·125	0·161	0·201
1·085	11·2	17	10·04	12·30	15·76	19·68	0·109	0·133	0·171	0·213
1·090	11·9	18	10·60	12·99	16·65	20·78	0·116	0·142	0·181	0·227
1·095	12·4	19	11·16	13·67	17·52	21·87	0·122	0·150	0·192	0·240
1·100	13·0	20	11·71	14·35	18·39	22·96	0·129	0·158	0·202	0·253
1·105	13·6	21	12·27	15·03	19·26	24·05	0·136	0·166	0·212	0·265
1·110	14·2	22	12·82	15·71	20·13	25·14	0·143	0·175	0·223	0·279
1·115	14·9	23	13·36	16·36	20·96	26·18	0·149	0·183	0·234	0·292
1·120	15·4	24	13·89	17·01	21·80	27·22	0·156	0·191	0·245	0·305
1·125	16·0	25	14·42	17·66	22·63	28·26	0·162	0·199	0·255	0·318
1·130	16·5	26	14·95	18·31	23·47	29·30	0·169	0·207	0·265	0·331
1·135	17·1	27	15·48	18·96	24·29	30·34	0·176	0·215	0·276	0·344
1·140	17·7	28	16·01	19·61	25·13	31·38	0·183	0·223	0·287	0·358
1·145	18·3	29	16·54	20·26	25·96	32·42	0·189	0·231	0·297	0·371
1·150	18·8	30	17·07	20·91	26·79	33·46	0·196	0·239	0·308	0·385
1·155	19·3	31	17·59	21·55	27·61	34·48	0·203	0·248	0·319	0·398
1·160	19·8	32	18·11	22·19	28·43	35·50	0·210	0·257	0·330	0·412
1·165	20·3	33	18·64	22·83	29·25	36·53	0·217	0·266	0·341	0·426
1·170	20·9	34	19·16	23·47	30·07	37·55	0·224	0·275	0·352	0·439
1·175	21·4	35	19·69	24·12	30·90	38·59	0·231	0·283	0·363	0·453
1·180	22·0	36	20·21	24·76	31·73	39·62	0·238	0·292	0·374	0·467
1·185	22·5	37	20·73	25·40	32·55	40·64	0·246	0·301	0·386	0·481
1·190	23·0	38	21·26	26·04	33·37	41·66	0·253	0·310	0·397	0·496
1·195	23·5	39	21·78	26·68	34·19	42·69	0·260	0·319	0·409	0·511
1·200	24·0	40	22·30	27·32	35·01	43·71	0·268	0·328	0·420	0·525
1·205	24·5	41	22·82	27·95	35·83	44·72	0·275	0·337	0·432	0·539
1·210	25·0	42	23·33	28·58	36·66	45·73	0·282	0·346	0·444	0·553
1·215	25·5	43	23·84	29·21	37·45	46·74	0·290	0·355	0·455	0·568
1·220	26·0	44	24·36	29·84	38·23	47·74	0·297	0·364	0·466	0·583
1·225	26·4	45	24·88	30·48	39·05	48·77	0·305	0·373	0·478	0·598
1·230	26·9	46	25·39	31·11	39·86	49·78	0·312	0·382	0·490	0·612
1·235	27·4	47	25·88	31·70	40·61	50·72	0·320	0·391	0·502	0·626
1·240	27·9	48	26·35	32·28	41·37	51·65	0·327	0·400	0·513	0·640
1·245	28·4	49	26·83	32·86	42·11	52·58	0·334	0·409	0·524	0·655
1·250	28·8	50	27·29	33·43	42·84	53·49	0·341	0·418	0·535	0·669
1·255	29·3	51	27·76	34·00	43·57	54·40	0·348	0·426	0·547	0·683
1·260	29·7	52	28·22	34·57	44·30	55·31	0·356	0·435	0·558	0·697
1·265	30·2	53	28·69	35·14	45·03	56·22	0·363	0·444	0·570	0·711
1·270	30·6	54	29·15	35·71	45·76	57·14	0·370	0·454	0·582	0·725
1·275	31·1	55	29·62	36·29	46·50	58·06	0·377	0·462	0·593	0·740
1·280	31·5	56	30·10	36·87	47·24	58·99	0·385	0·472	0·605	0·755
1·285	32·0	57	30·57	37·45	47·99	59·92	0·393	0·481	0·617	0·770
1·290	32·4	58	31·04	38·03	48·73	60·85	0·400	0·490	0·629	0·785
1·295	32·8	59	31·52	38·61	49·47	61·78	0·408	0·500	0·641	0·800
1·300	33·3	60	31·99	39·19	50·21	62·70	0·416	0·510	0·653	0·815
1·305	33·7	61	32·46	39·77	50·96	63·63	0·424	0·519	0·665	0·830
1·310	34·2	62	32·94	40·35	51·71	64·56	0·432	0·529	0·677	0·845
1·315	34·6	63	33·41	40·93	52·45	65·45	0·439	0·538	0·689	0·860
1·320	35·0	64	33·88	41·50	53·18	66·40	0·447	0·548	0·702	0·876
1·325	35·4	65	34·35	42·08	53·92	67·33	0·455	0·557	0·714	0·892
1·330	35·8	66	34·80	42·66	54·67	68·26	0·462	0·567	0·727	0·908
1·335	36·2	67	35·27	43·20	55·36	69·12	0·471	0·577	0·739	0·923
1·340	36·6	68	35·71	43·74	56·05	69·98	0·479	0·586	0·751	0·938

Specific Gravity of Sulphuric Acid Solutions—*Continued.*

Sp. Gr at $\frac{15^\circ}{4^\circ}$ (*in vacuo.*)	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142 Tw.	Acid of 106° Tw.
1·345	37·0	69	36·14	44·28	56·74	70·85	0·486	0·596	0·763	0·953
1·350	37·4	70	36·58	44·82	57·43	71·71	0·494	0·605	0·775	0·968
1·355	37·8	71	37·02	45·35	58·11	72·56	0·502	0·614	0·787	0·983
1·360	38·2	72	37·45	45·88	58·79	73·41	0·509	0·624	0·800	0·998
1·365	38·6	73	37·89	46·41	59·48	74·26	0·517	0·633	0·812	1·014
1·370	39·0	74	38·32	46·94	60·15	75·10	0·525	0·643	0·824	1·029
1·375	39·4	75	38·75	47·47	60·83	75·95	0·533	0·653	0·836	1·044
1·380	39·8	76	39·18	48·00	61·51	76·80	0·541	0·662	0·849	1·060
1·385	40·1	77	39·62	48·53	62·19	77·65	0·549	0·672	0·861	1·075
1·390	40·5	78	40·05	49·06	62·87	78·50	0·557	0·682	0·873	1·091
1·395	40·8	79	40·48	49·59	63·55	79·34	0·564	0·692	0·886	1·107
1·400	41·2	80	40·91	50·11	64·21	80·18	0·573	0·702	0·899	1·123
1·405	41·6	81	41·33	50·63	64·88	81·01	0·581	0·711	0·912	1·138
1·410	42·0	82	41·76	51·15	65·55	81·86	0·589	0·721	0·924	1·154
1·415	42·3	83	42·17	51·66	66·21	82·66	0·597	0·730	0·937	1·170
1·420	42·7	84	42·57	52·15	66·82	83·44	0·604	0·740	0·949	1·185
1·425	43·1	85	42·96	52·63	67·44	84·21	0·612	0·750	0·961	1·200
1·430	43·4	86	43·36	53·11	68·06	84·98	0·620	0·759	0·973	1·215
1·435	43·8	87	43·75	53·59	68·68	85·74	0·628	0·769	0·986	1·230
1·440	44·1	88	44·14	54·07	69·29	86·51	0·636	0·779	0·998	1·246
1·445	44·4	89	44·53	54·55	69·90	87·28	0·643	0·789	1·010	1·261
1·450	44·8	90	44·92	55·03	70·52	88·05	0·651	0·798	1·023	1·277
1·455	45·1	91	45·31	55·50	71·12	88·80	0·659	0·808	1·035	1·292
1·460	45·4	92	45·69	55·97	71·72	89·55	0·667	0·817	1·047	1·307
1·465	45·8	93	46·07	56·43	72·31	90·29	0·675	0·827	1·059	1·323
1·470	46·1	94	46·45	56·90	72·91	91·04	0·683	0·837	1·072	1·338
1·475	46·4	95	46·83	57·37	73·51	91·79	0·691	0·846	1·084	1·354
1·480	46·8	96	47·21	57·83	74·10	92·53	0·699	0·856	1·097	1·370
1·485	47·1	97	47·57	58·28	74·68	93·25	0·707	0·865	1·109	1·385
1·490	47·4	98	47·95	58·74	75·27	93·98	0·715	0·876	1·122	1·400
1·495	47·8	99	48·34	59·22	75·88	94·75	0·723	0·885	1·134	1·417
1·500	48·1	100	48·73	59·70	76·50	95·52	0·731	0·896	1·147	1·433
1·505	48·4	101	49·12	60·18	77·12	96·29	0·739	0·906	1·160	1·449
1·510	48·7	102	49·51	60·65	77·72	97·04	0·748	0·916	1·174	1·465
1·515	49·0	103	49·89	61·12	78·32	97·79	0·756	0·926	1·187	1·481
1·520	49·4	104	50·28	61·59	78·93	98·54	0·764	0·936	1·199	1·498
1·525	49·7	105	50·66	62·06	79·52	99·30	0·773	0·946	1·213	1·514
1·530	50·0	106	51·04	62·53	80·13	100·05	0·781	0·957	1·226	1·531
1·535	50·3	107	51·43	63·00	80·73	100·80	0·789	0·967	1·239	1·547
1·540	50·6	108	51·78	63·43	81·28	101·49	0·797	0·977	1·252	1·563
1·545	50·9	109	52·12	63·85	81·81	102·16	0·805	0·987	1·264	1·579
1·550	51·2	110	52·46	64·26	82·34	102·82	0·813	0·996	1·276	1·593
1·555	51·5	111	52·79	64·67	82·87	103·47	0·821	1·006	1·289	1·609
1·560	51·8	112	53·22	65·20	83·50	104·30	0·830	1·017	1·303	1·627
1·565	52·1	113	53·59	65·65	84·08	105·03	0·839	1·027	1·316	1·644
1·570	52·4	114	53·95	66·09	84·64	105·73	0·847	1·038	1·329	1·660
1·575	52·7	115	54·32	66·53	85·21	106·42	0·856	1·048	1·343	1·677
1·580	53·0	116	54·65	66·95	85·78	107·10	0·864	1·058	1·356	1·692
1·585	53·3	117	55·03	67·40	86·34	107·85	0·872	1·068	1·369	1·709
1·590	53·6	118	55·37	67·83	86·88	108·52	0·880	1·078	1·382	1·726
1·595	53·9	119	55·73	68·26	87·44	109·21	0·889	1·089	1·395	1·742
1·600	54·1	120	56·09	68·70	88·00	109·92	0·897	1·099	1·409	1·759
1·605	54·4	121	56·44	69·13	88·55	110·61	0·906	1·110	1·422	1·775

Specific Gravity of Sulphuric Acid Solutions—*Continued.*

Sp. Gr. at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·610	54·7	122	56·79	69·56	89·10	111·30	0·914	1·120	1·435	1·792
1·615	55·0	123	57·15	70·00	89·66	112·00	0·923	1·131	1·449	1·810
1·620	55·2	124	57·49	70·42	90·20	112·68	0·931	1·141	1·462	1·825
1·625	55·5	125	57·84	70·85	90·74	113·35	0·940	1·151	1·473	1·842
1·630	55·8	126	58·18	71·27	91·29	114·02	0·948	1·162	1·489	1·859
1·635	56·0	127	58·53	71·70	91·83	114·71	0·957	1·172	1·502	1·875
1·640	56·3	128	58·88	72·12	92·38	115·40	0·966	1·182	1·516	1·892
1·645	56·6	129	59·22	72·55	92·92	116·06	0·975	1·193	1·529	1·909
1·650	56·9	130	59·57	72·96	93·45	116·72	0·983	1·204	1·543	1·926
1·655	57·1	131	59·92	73·40	94·02	117·44	0·992	1·215	1·557	1·944
1·660	57·4	132	60·26	73·81	94·54	118·11	1·000	1·225	1·570	1·960
1·665	57·7	133	60·61	74·24	95·08	118·77	1·009	1·230	1·584	1·977
1·670	57·9	134	60·95	74·66	95·62	119·36	1·017	1·246	1·598	1·995
1·675	58·2	135	61·29	75·08	96·16	120·11	1·027	1·259	1·611	2·012
1·680	58·4	136	61·63	75·50	96·69	120·50	1·035	1·268	1·625	2·029
1·685	58·7	137	61·93	75·94	97·21	121·38	1·043	1·278	1·638	2·046
1·690	58·9	138	62·29	76·38	97·77	122·08	1·053	1·289	1·652	2·064
1·695	59·2	139	62·64	76·76	98·32	122·77	1·062	1·301	1·667	2·082
1·700	59·5	140	63·00	77·17	98·89	123·47	1·071	1·312	1·681	2·100
1·705	59·7	141	63·35	77·60	99·44	124·16	1·080	1·323	1·696	2·117
1·710	60·0	142	63·70	78·04	100·00	124·86	1·089	1·334	1·710	2·136
1·715	60·2	143	64·07	78·48	100·56	125·57	1·099	1·346	1·725	2·154
1·720	60·4	144	64·43	78·92	101·13	126·27	1·108	1·357	1·739	2·172
1·725	60·6	145	64·78	79·36	101·69	126·98	1·118	1·369	1·754	2·191
1·730	60·9	146	65·14	79·80	102·25	127·68	1·127	1·381	1·769	2·209
1·735	61·1	147	65·50	80·24	102·82	128·38	1·136	1·392	1·784	2·228
1·740	61·4	148	65·86	80·68	103·38	129·09	1·146	1·404	1·799	2·247
1·745	61·6	149	66·22	81·12	103·95	129·79	1·156	1·416	1·814	2·265
1·750	61·8	150	66·58	81·56	104·52	130·49	1·165	1·427	1·829	2·284
1·755	62·1	151	66·94	82·00	105·08	131·20	1·175	1·439	1·845	2·303
1·760	62·3	152	67·30	82·44	105·64	131·90	1·185	1·451	1·859	2·321
1·765	62·5	153	67·76	83·01	106·31	132·80	1·196	1·465	1·877	2·344
1·770	62·8	154	68·17	83·51	106·91	133·61	1·207	1·478	1·894	2·365
1·775	63·0	155	68·60	84·02	107·62	134·43	1·218	1·491	1·911	2·386
1·780	63·2	156	68·98	84·50	108·27	135·20	1·228	1·504	1·928	2·407
1·785	63·5	157	69·47	85·10	109·05	136·16	1·240	1·519	1·947	2·432
1·790	63·7	158	69·96	85·70	109·82	137·14	1·252	1·534	1·965	2·455
1·795	64·0	159	70·45	86·30	110·58	138·08	1·265	1·549	1·983	2·479
1·800	64·2	160	70·96	86·92	111·32	139·06	1·277	1·565	2·003	2·503
1·805	64·4	161	71·50	87·60	112·25	140·16	1·291	1·581	2·026	2·530
1·810	64·6	162	72·08	88·30	113·15	141·28	1·305	1·598	2·048	2·558
1·815	64·8	163	72·96	89·16	114·21	142·65	1·322	1·618	2·074	2·589
1·820	65·0	164	73·51	90·05	115·33	144·08	1·338	1·639	2·099	2·622
1·821	...	...	73·63	90·20	115·59	144·32	1·341	1·643	2·104	2·628
1·822	65·1	...	73·80	90·40	115·84	144·64	1·345	1·647	2·110	2·635
1·823	...	...	73·96	90·60	116·10	144·96	1·348	1·651	2·116	2·643
1·824	65·2	...	74·12	90·80	116·35	145·28	1·352	1·656	2·122	2·650
1·825	...	165	74·29	91·00	116·61	145·60	1·356	1·661	2·128	2·657
1·826	65·3	...	74·49	91·25	116·93	146·00	1·360	1·666	2·135	2·666
1·827	...	...	74·69	91·50	117·25	146·40	1·364	1·671	2·142	2·675
1·828	65·4	...	74·86	91·70	117·51	146·72	1·368	1·676	2·148	2·682
1·829	...	...	75·03	91·90	117·76	147·04	1·372	1·681	2·154	2·689
1·830	...	166	75·19	92·10	118·02	147·36	1·376	1·685	2·159	2·696

Specific Gravity of Sulphuric Acid Solutions—*Continued.*

Sp. Gr. at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·831	65·5	...	75·46	92·43	118·41	147·88	1·382	1·692	2·169	2·708
1·832	...	...	75·69	92·70	118·73	148·32	1·336	1·698	2·176	2·717
1·833	65·6	...	75·89	92·97	119·07	148·73	1·391	1·704	2·184	2·727
1·834	...	...	76·12	93·25	119·43	149·18	1·396	1·710	2·191	2·736
1·835	65·7	167	76·38	93·56	119·84	149·70	1·402	1·717	2·200	2·747
1·836	...	...	76·57	93·90	120·19	150·08	1·406	1·722	2·207	2·755
1·837	...	...	76·90	94·25	120·71	150·72	1·412	1·730	2·217	2·769
1·838	65·8	...	77·23	94·60	121·22	151·36	1·419	1·739	2·228	2·782
1·839	...	...	77·55	95·00	121·74	152·00	1·426	1·748	2·239	2·795
1·840	65·9	168	78·04	95·60	122·51	152·96	1·436	1·759	2·254	2·814
1·8405	...	...	78·33	95·95	122·96	153·52	1·451	1·765	2·262	2·825
1·8410	...	...	78·69	96·38	123·45	154·20	1·448	1·774	2·273	2·838
1·8415	...	...	79·47	97·35	124·69	155·74	1·463	1·792	2·296	2·867
1·8410	...	...	80·16	98·20	125·84	157·12	1·476	1·808	2·317	2·893
1·8405	...	...	80·43	98·52	126·18	157·62	1·481	1·814	2·325	2·903
1·8400	...	...	80·59	98·72	126·44	157·94	1·483	1·816	2·327	2·906
1·8395	...	...	80·63	98·77	126·50	158·00	1·484	1·817	2·328	2·907
1·8390	...	...	80·93	99·12	126·99	158·60	1·488	1·823	2·336	2·917
1·8385	...	...	81·08	99·31	127·35	158·90	1·490	1·826	2·339	2·921

A table giving the relationship between the percentage content and the readings of the hydrometer employed in the United States has been published by Elliot.[1]

The tables calculated by Richmond[2] and by Marshall[3] from Pickering's measurements,[4] and which they regard as very exact, are not really so, since Pickering only employed a relative and not an absolute unit for his determinations; the figures consequently require to be corrected by multiplying by the factor 0·9974, as given by the German Standards Commission.[5]

Temperature Correction.

Since in practice the specific gravity determinations are only seldom made at exactly 15° C., it is necessary to have a means of correcting readings made at a higher or lower temperature.

Lunge has compiled a table, based on an extended series of observations, for this purpose. An abridged form of the complete table is given below.[6]

A very complete table has also been published by the German Standards Commission.

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[1] *J. Soc. Chem. Ind.*, 1898, **17**, 45. [2] *Ibid.*, 1890, **9**, 479. [3] *Ibid.*, 1899, **10**, 6.

[4] *J. Chem. Soc.*, 1890, **57**, 63 and 331. [5] *Report*, 1904, p. 221.

[6] The complete table is given in *The Alkali Makers' Handbook*, Lunge and Hurter, 2nd edition, pp. 105-108.

Lunge's table agrees very well with the latter down to a sp. gr. 1·100 = about 15 per cent. H_2SO_4. The table is inapplicable for weaker acids, owing to an error which cannot now be traced; it is, however, seldom likely to be required for such weak acids in practice.

Table showing the Influence of Temperature on the Specific Gravity of Sulphuric Acid.

a. Specific gravity at 15°/4°; under *t*, changes in specific gravity at the temperature *t*.

a.	*t.* 0°	*t.* 10°	*t.* 20°	*t.* 30°	*t.* 40°	*t.* 50°	*t.* 60°
1·840	+0·015	+0·005	−0·005	−0·015	−0·025	−0·034	−0·044
1·820	16	5	5	16	26	37	47
1·800	17	5	5	16	27	37	47
1·780	17	5	5	16	27	37	47
1·760	16	5	5	16	26	36	47
1·740	16	5	5	15	25	35	45
1·720	15	5	5	15	25	35	44
1·700	15	5	5	14	24	33	43
1·680	15	5	5	14	24	33	42
1·660	14	5	5	14	23	32	41
1·640	14	5	4	14	23	32	40
1·620	14	4	4	14	22	31	40
1·600	14	4	4	13	22	31	39
1·580	14	4	4	13	22	30	39
1·560	13	4	4	13	21	30	38
1·540	13	4	4	13	21	30	38
1·520	13	4	4	13	21	29	37
1·500	13	4	4	12	21	29	37
1·480	13	4	4	12	20	28	36
1·460	12	4	4	12	20	28	36
1·440	12	4	4	12	20	28	35
1·420	12	4	4	12	19	27	35
1·400	12	4	4	12	19	27	34
1·380	12	4	4	11	19	27	34
1·360	11	4	4	11	19	26	34
1·340	11	4	4	11	19	26	33
1·320	11	3	4	11	18	26	33
1·300	11	3	3	11	18	26	33
1·280	11	3	3	11	18	25	33
1·260	11	3	3	11	18	25	32
1·240	11	3	3	10	18	24	32
1·220	10	3	3	10	17	24	31
1·200	10	3	3	10	17	23	30
1·180	10	3	3	10	16	23	29
1·160	9	3	3	9	15	22	28
1·140	8	3	3	8	14	20	27
1·120	8	2	2	8	14	19	25
1·100	7	2	2	7	13	18	24
1·080	6	2	2	7	12	17	23
1·060	5	2	2	6	10	16	21
1·040	3	1	1	5	9	14	20
1·020	2	1	1	4	8	13	18
1·010	2	1	1	4	7	12	17

For temperatures below 15° the values given in the column *t* must, of course, be subtracted from the observed reading; for temperatures above 15° the corrections must be added to give the value at 15°. A table has also been calculated by Fuchs[1] for this correction.

The following table, p. 357, worked out by the *Chemische Fabrik*, Griesheim, will be found useful in many cases.

It is to be noted that the values given in all the above tables only hold good for chemically pure acid. In commercial acids the specific gravities at the highest concentrations are appreciably higher than the values given in the tables, but the variations between acids made at different works are too irregular to permit of a table being prepared for such acids. The specific gravity is influenced in the case of nitrous vitriol by the percentage of nitrous acid present, and in the case of chamber and concentrated acids by the presence of sulphurous acid, lead sulphate, nitrogen oxides, arsenic, and iron. The quantity of these usually present in sulphuric acid is too slight to markedly affect the specific gravity; nevertheless exceptional cases may occur in which the acid is strongly contaminated with iron, aluminium, or sodium salts. The iron may result, for example, from pyrites dust, the aluminium from the packing of the Glover tower, or from the fireclay frequently employed for temporarily repairing leaks, the sodium salts from solutions of Chili saltpetre or Glauber's salts, which sometimes get into the chambers through carelessness. Nitric acid, which occurs in appreciable quantity in sulphuric acid recovered from spent, nitrating acids, also causes an increase in the specific gravity.

The influence of impurities on the specific gravity of sulphuric acid has been dealt with by Lunge,[2] also in a recent paper by Marshall,[3] and in special detail by the German Standards Commission.[4] According to the Commission the Glover acid, as might be expected, is the most impure, the differences between the actual percentages found by analysis and those obtained by calculation from the tables varying from 0·5 to 1·87 per cent. "Commercially pure" chamber acid showed differences of 0·01 to 0·26 per cent.; acids of 142° Tw., of (exceptionally) 0·03 to 1·55 per cent.; acids of 168° Tw. made from chamber acid, differences of 0·24 to 0·76 per cent., in one instance only 0·02 per cent.; whilst acid free from arsenic differed from the actual percentage by from 0·09 to 0·65 per cent. Acids made by the contact process showed differences of only 0·02 to 0·23 per cent., and acid manufactured from sulphuretted hydrogen of only 0·02 to 0·18 per cent.

Since the changes in specific gravity with strength are very slight in the case of high-strength acids, and as it is just in these acids that the impurities, always present in commercial acids, have the greatest effect on the specific gravity, which is increased by their presence, the tables should only be used for guidance in the works

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[1] *Z. angew. Chem.*, 1898, **11**, 950.

[2] *Sulphuric Acid and Alkali*, vol. i., p. 189 *et seq.*

[3] *J. Soc. Chem. Ind.*, 1902, **21**, 1503.

[4] Report, 1904, **5**, p. 243 *et seq.*

Reduction of the Hydrometer Readings for Sulphuric Acid between 65° and 66° B. (164° and 168° Tw.) to 15° C.

The hydrometer reading is taken from the first vertical column, and the observed temperature from the top line. The reading which lies vertically below the observed temperature and on the line containing the observed specific gravity gives the specific gravity at 15°.

° B.	10	11°	12°	13	14°	15°	16°	17°	18°	19°	20	21	22°	23	24	25°	26°	27	28°	29	30°
65·00	64·80	64·84	64·88	64·92	64·96	65·00	65·04	65·08	65·12	65·16	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60
65·10	64·90	64·94	64·98	65·02	65·06	65·10	65·14	65·18	65·22	65·26	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70
65·20	65·00	65·04	65·08	65·12	65·16	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80
65·30	65·10	65·14	65·18	65·22	65·26	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90
65·40	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00
65·50	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10
65·60	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20
65·70	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10	66·14	66·18	66·22	66·26	66·30
65·80	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20	66·24	66·28	66·32	66·36	66·40
65·90	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10	66·14	66·18	66·22	66·26	66·30	66·34	66·38	66·42	66·46	66·50
66·00	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20	66·24	66·28	66·32	66·36	66·40	66·44	66·48	66·52	66·56	66·60

for acids of over 90 per cent. strength; for selling purposes, actual analyses should always be made.

Melting Points of Sulphuric Acid. Knietsch.[1]

Enlarged by Lunge by the addition of the corresponding percentage of H_2SO_4.

The melting points given in the table are the temperatures which remain constant during the period of complete crystallisation; that is, from the temperature at which crystals begin to appear in the cooled acid until the stage when the mass becomes solid after removal from the freezing mixture.

Sulphuric Acid.								
Total SO_3 per cent.	H_2SO_4 per cent.	Melting-Point. ° C.	Total SO_3 per cent.	H_2SO_4 per cent.	Melting-Point. ° C.	Total SO_3 per cent.	H_2SO_4 per cent.	Melting-Point. ° C.
1	1·22	− 0·6	23	28·17	− 40·1	80	98·00	+ 3·0
2	2·45	− 1·0			Under	81	99·25	+ 7·0
3	3·67	− 1·7	...	...	− 40·0	81·63	100·00	+ 10·0
4	4·90	− 2·0	61	74·72	− 40·0	82	...	+ 8·2
5	6·12	− 2·7	62	75·95	− 20·0	83	...	− 0·8
6	7·35	− 3·6	63	77·17	− 11·5	84	...	− 9·2
7	8·57	− 4·4	64	78·40	− 4·8	85	...	− 11·0
8	9·80	− 5·3	65	79·62	− 4·2	86	...	− 2·2
9	11·02	− 6·0	66	80·85	+ 1·2	87	...	+ 13·5
10	12·25	− 6·7	67	82·07	+ 8·0	88	...	+ 26·0
11	13·47	− 7·2	68	83·39	+ 8·0	89	...	+ 34·2
12	14·70	− 7·9	69	84·52	+ 7·0	90	...	+ 34·2
13	15·92	− 8·2	70	85·75	+ 4·0	91	...	+ 25·8
14	17·15	− 9·0	71	86·97	− 1·0	92	...	+ 14·2
15	18·37	− 9·3	72	88·20	− 7·2	93	...	+ 0·8
16	19·60	− 9·8	73	89·42	− 16·2	94	...	+ 4·5
17	20·82	− 11·4	74	90·65	− 25·0	95	...	+ 14·8
18	22·05	− 13·2	75	91·87	− 34·0	96	...	+ 20·3
19	23·27	− 15·2	76*	93·10	− 32·0	97	...	+ 29·2
20	24·50	− 17·1	77*	94·83	− 28·2	98	...	+ 33·8
21	25·72	− 22·5	78*	95·05	− 16·5	99	...	+ 36·0
22	26·95	− 31·0	79	96·77	− 5·2	100	...	+ 40·0

* So-called 168° Tw.

Boiling Points of Sulphuric Acid.[2]

Per cent. H_2SO_4.	Specific Gravity.	Degrees Beaumé.	Boiling-Point. ° C.	Per cent. H_2SO_4.	Specific Gravity.	Degrees Beaumé.	Boiling-Point. ° C.	Per cent. H_2SO_4.	Specific Gravity.	Degrees Beaumé.	Boiling-Point. ° C.
5	1·031	4·2	101	56	1·459	45·4	133	82	1·758	62·2	218·5
10	1·069	9·2	102	60	1·503	48·3	141·5	84	1·773	63·0	227
15	1·107	13·9	103·5	62·5	1·530	50·0	147	86	1·791	63·8	238·5
20	1·147	18·5	105	65	1·557	51·6	153·5	88	1·807	64·4	251·5
25	1·184	22·4	106·5	67·5	1·585	53·3	161	90	1·818	65·0	262·5
30	1·224	26·4	108	70	1·615	55·0	170	91	1·824	65·3	268
35	1·265	30·2	110	72	1·639	56·3	174·5	92	1·830	65·45	274·5
40	1·307	33·9	114	74	1·661	57·4	180·5	93	1·834	65·65	281·5
45	1·352	37·6	118·5	76	1·688	58·8	189	94	1·837	65·8	288·5
50	1·399	41·1	124	78	1·710	60·0	199	95	1·840	65·9	295
53	1·428	43·3	128·5	80	1·733	61·0	207	...	...	...	...

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[1] *Ber.*, 1901, **34**, 4100.

[2] Lunge, *Ber.*, 1878, **11**, 370.

QUALITATIVE EXAMINATION OF SULPHURIC ACID FOR IMPURITIES

The impurities likely to be present in ordinary commercial sulphuric acid are:—Sulphates of sodium (less frequently potassium), ammonium, calcium, aluminium, iron and lead, exceptionally also of zinc and copper; arsenic, selenium, thallium, titanium, nitrogen oxides, hydrochloric acid, sulphurous acid, and hydrofluoric acid.

Acidum sulfuricum purissimum is, according to Krauch,[1] tested for fixed residue, nitric acid, selenium, reducing substances, lead, other metals, arsenic, ammonia, and the halogens.

General examination for gaseous impurities (Warington). Two kilos of the undiluted acid are thoroughly shaken in a flask, of a capacity equal to twice the volume of the acid, so as to saturate the air in the flask with the gases dissolved in the acid. The atmosphere in the flask is then tested for sulphurous acid by iodised starch paper and for gaseous oxides of nitrogen by potassium iodide starch paper. Any blue coloration produced by the latter gases will not be destroyed by sulphurous acid unless this is present in considerable excess. Sulphuretted hydrogen reacts like sulphurous acid in this test.

Sulphurous acid. This gas will decolorise a starch solution rendered faintly blue by iodine; or it may be converted into sulphuretted hydrogen by means of zinc or aluminium, and examined by lead acetate paper or by an alkaline solution of sodium nitroprusside. The latter is a very delicate test.

Hydrochloric acid. Two g. are diluted to 30 c.c., and a few drops of silver nitrate solution added; in the case of acid. sulfuric. puriss no turbidity should result. The hydrochloric acid present in ordinary commercial vitriol arises from the sodium chloride present in the nitre.

The qualitative examination for traces of Nitrogen Acids is best made with diphenylamine. The diphenylamine is dissolved in about 100 parts of pure sulphuric acid, or failing this, in an acid freed from nitrogen compounds by boiling with the addition of a very small amount of ammonium sulphate, and the solution diluted with about $\frac{1}{10}$ of its volume of water. The solution may be used at once, or may be kept if desired: it becomes, however, discoloured and less sensitive after some time. In testing concentrated sulphuric acid for nitrogen acids about 2 c.c. of the acid are placed in a test-tube or conical test-glass, and about 1 c.c. of the diphenylamine solution added carefully so that the two layers only mix slowly; in the case of weaker acids or other solutions of lower specific gravity the order is reversed, and the heavier diphenylamine solution placed below. The slightest trace of nitrogen acids is

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[1] *The Testing of Chemical Reagents for Purity*, p. 305.

shown by the development of a beautiful blue colour at the junction of the two solutions.[1]

In the presence of *Selenium*, which also gives the above reaction with diphenylamine, nitrogen acids, if present in somewhat large quantity, may be recognised by the decolorising effect on indigo solution, whilst if only present in traces they may be detected by the reddening produced in a solution of brucine sulphate. Selenium is detected by the formation of a brownish-red precipitate on the addition of a concentrated solution of ferrous sulphate to the vitriol; this precipitate cannot be confused with the simple coloration produced by nitric oxide. The detection of nitrogen acids by means of ferrous sulphate has been described above (p. 341).

Nitrous acid can be detected by a number of very delicate reactions, which are not given by nitric acid. These include the blue coloration produced in potassium iodide starch solution, or still better in zinc iodide starch solution. Its presence is detected with especial ease by the formation of azo-colours, a reaction first discovered by Griess, who recommended the use of metaphenylenediamine, which gives rise to a yellow coloration, and also the still more sensitive reaction with sulphanilic acid and α-naphthylamine, which produces a rose coloration. The latter reagent has the disadvantage that the naphthylamine solution, even when prepared from a perfectly white salt, becomes dark coloured after a relatively short time, and as a result loses its sensitiveness. Further, in very dilute solutions, such as 1 in 1000 millions, the reaction takes place so slowly that it is impossible to be quite certain that the coloration arises from the substance tested and not from nitrous acid present in the air; the time may be appreciably shortened by warming the solution, but even in this case fifteen to twenty minutes may be necessary.

Ilosvay[2] found that by using acetic acid instead of sulphuric acid or hydrochloric acid, the time required for the reaction is very much decreased, and that at the same time the colour is developed to a much greater extent. He overcomes the difficulty of the discoloration of the naphthylamine by adopting the following method of preparing the solution:—0·5 g. of sulphanilic acid is dissolved in 150 c.c. of dilute acetic acid and 0·1 g. of solid naphthylamine is boiled with 20 c.c. of water, the colourless solution poured off from the bluish-violet residue, and 150 c.c. of dilute acetic acid added to this solution. In testing, a few c.c. of the sulphanilic acid solution are added to about 20 c.c. of the solution to be examined, the mixture warmed to 70° to 80°, and the naphthylamine solution then added. In the presence of one part of nitrous acid in 1000 million parts of solution the red coloration, due to the azo-colour produced, appears in about a minute; if the nitrous acid

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[1] *Cf.* Lunge, *Z. angew. Chem.*, 1894, **7**, 345.

[2] *Bull. Soc. Chim.*, 1889 [3], **2**, 317.

be present in relatively large amount, about 1 : 1000, only a yellow solution is obtained unless a concentrated solution of naphthylamine be employed.

Lunge[1] mixes the solutions of sulphanilic acid and naphthylamine prepared according to Ilosvay's directions, together, and keeps the mixture in a well-stoppered bottle. It is unnecessary to exclude light from the mixed solutions, but it is essential to prevent access of air, since this may possibly contain nitrous acid as an impurity. By thus combining the two reagents in a single solution, any contamination by nitrous acid from the atmosphere is at once evidenced by the red colour of the solution. A solution that has become red may be very quickly rendered fit for use by shaking with zinc dust and filtering. With the reagents ready mixed, the reaction may also be hastened by warming the solution to 70° to 80°. (Cf. *infra*, under the quantitative application of the method.)

Riegler[2] recommends the use of naphthionic acid or sodium naphthionate and β-naphthol, but this has no advantage over Griess' reagents, and according to Riegler himself is not so sensitive (1 : 100 million). This reagent can be used colorimetrically.

H. Erdmann[3] employs sulphanilic acid in hydrochloric acid solution, or, still better, *p*-amino-benzoic ester, followed by the acid sodium salt of 1-amino-8-naphthol-4-6-disulphonic acid (also known as amino-naphthol-*K* acid, and sold under the name "Water-analysis reagent—Bagdad"). The coloration produced by this reagent is a bright wine-red. Mennicke[4] has defended this method against certain adverse criticism, and states that one part of sodium nitrite in 2000 million parts of water can be detected by its aid.

Brucine in sulphuric acid solution reacts only with nitric acid and not with nitrous acid when sulphuric acid is present in large excess; nitrous acid only gives a coloration if the solution contains at least two parts of water to each part of sulphuric acid. Consequently, to test only for nitric acid, the solution should contain sulphuric acid equal to 2/3 of its volume, and the test be carried out by adding 1 c.c. of a solution of 0·2 g. brucine in 100 c.c. strong sulphuric acid, to 50 c.c. of the solution to be examined. In the presence of 0·01 mg. nitrate-nitrogen, a red colour—subsequently passing through orange to a golden yellow[5]—results.

Hydrofluoric acid may be detected by warming the acid in a platinum dish, covered with a glass plate coated with wax in which figures have been scratched.

Ammonia. Two g. of the acid are diluted with about 30 c.c. of water, the solution made alkaline by the addition of a potassium

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[1] *Z. angew. Chem.*, 1889, **2**, 666.

[2] *Z. anal. Chem.*, 1896, **35**, 677; 1897, **36**, 306, 377, 665.

[3] *Z. angew. Chem.*, 1900, **13**, 33.

[4] *Ibid.*, 1900, **13**, 235 and 711.

[5] *Cf.* Winkler, *Z. angew. Chem.*, 1901, **14**, 170; and, Lunge, *ibid.*, 1901, **14**, 241.

hydroxide solution containing 3 to 4 g. pure hydroxide, and ten to fifteen drops of Nessler's reagent added; no distinctly yellow or brownish-red coloration should result.

Krauch states that by this method 1 mg. NH_3 in 100 g. concentrated sulphuric acid will produce a distinct yellow coloration and turbidity.

Solid impurities. Lead is shown by any turbidity which results on the addition of five volumes of strong alcohol to one volume of the acid; simple dilution with water is sufficient if the lead be present in considerable quantity. The presence of lead may be confirmed by examining the precipitate in the blowpipe flame, etc.

Iron. The acid is boiled, after the addition of one drop of pure nitric acid, diluted slightly, and when cold, treated with an excess of thiocyanate solution. A blank test should always be made with the nitric acid employed, to make sure that any red coloration produced is not due to this.

Venable[1] employs a mixture of cobalt nitrate and strong hydrochloric acid. Traces of ferric salts change the blue colour of the solution to green; ferrous salts do not affect it.

Selenium is recognised by the red coloration and subsequent red precipitate produced by the addition of ferrous sulphate to the solution; the reaction is hastened by warming. Sulphurous acid is a better reagent than ferrous sulphate for this test. The presence of 0·01 per cent. of selenium is shown, after some hours, by either reagent. Codeine may also be used, but it is less sensitive than the preceding reagents, requiring 0·5 per cent. of selenium to show a reaction.[2] Selenic acid cannot be tested for by any of these reagents, but it may be detected by means of acetylene, which also reacts with selenious acid, and produces a red coloration in the presence of only 0·001 per cent. of selenium; a little hydrochloric acid hastens the separation of the selenium, which is soluble in hot sulphuric acid, forming a green solution.

Detection and Approximate Estimation of Arsenic

Examination for this impurity is always important, and it is absolutely necessary in all cases where the acid is sold as pure, or is intended for use in the preparation of substances such as glucose, tartaric acid, mineral water, yeast, etc., which either directly or indirectly may be used as food-stuffs. Sulphuric acid, prepared from pyrites, unless specially purified, usually contains from 0·1 to 0·2 per cent. of arsenious oxide, and, in exceptional cases, up to 1 per cent. and more.

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[1] *Z. anal. Chem.*, 1889, **28**, 699.

[2] Jouve, *Chem. Centr.*, 1901, **I.**, 1389; and, Orlow, *ibid.*, 1901, **1**, 480.

Very special attention has been directed to the presence of arsenic in sulphuric acid, owing to the numerous and in some instances fatal cases of arsenical poisoning that occurred in the year 1900. It was found that these cases arose from the consumption of beer, in the brewing of which glucose containing arsenic had been employed, the arsenic in the glucose being traced in turn to the sulphuric acid used in its manufacture. The investigation into the origin of this poisoning led to the publication of much important work on the detection and estimation of arsenic in various materials.[1]

Of the various methods of testing for arsenic, that of Marsh, more recently and correctly known as the Marsh-Berzelius test, is by far the most generally employed; the Reinsch and the Gutzeit methods are also largely used.

As a sequel to the outbreak of arsenical poisoning referred to above, a joint committee of the Society of Chemical Industry and of the Society of Public Analysts was appointed in 1901, to investigate the various methods for the detection and approximate estimation of arsenic in beer, brewers' materials, food-stuffs, and fuels;[2] this committee reported in favour of the Marsh-Berzelius test as the most reliable and generally applicable method.

According to Hehner,[3] ordinary pyrites vitriol contains on the average 0·2 per cent. of arsenious acid (As_2O_3); such acid, after purification, he considers permissible for use in the preparation of foods and for the other purposes mentioned above, provided that the arsenic left in does not exceed 0·05 mg. As_2O_3 in 10 g. of the acid, that is, one part As_2O_3 in 200,000 parts of acid. Very frequently the amount of arsenic remaining after purification is less than this limiting value, but no acid prepared from pyrites, and perhaps not even that from Sicilian brimstone, is absolutely free from arsenic; on the other hand, such freedom might be expected in acid made by the "contact process" when platinum is employed as the contact material. Acid prepared by the ferric oxide contact process is not free from arsenic (Conroy). Arsenic present to the extent of 0·001 mg. may be detected and estimated without special difficulty.

A. The Marsh-Berzelius Test.

The actual test, as proposed by Marsh in 1827, consisted in the formation of a dark stain on a piece of cold porcelain brought into a burning mixture of hydrogen and arseniuretted hydrogen. For more exact purposes, this is generally combined with the Berzelius reaction by heating the arsenical hydrogen gas during its passage through a

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[1] *Cf.* Report of the Royal Commission on Arsenical Poisoning, 1903; *J. Soc. Chem. Ind.* 1904, **23**, 159.

[2] The full Report of the Committee is published in the *J. Soc. Chem. Ind.*, 1902, **21**, 94.

[3] *J. Soc. Chem. Ind.*, 1901, **20**, 188.

glass tube, and so effecting a decomposition of the arseniuretted hydrogen with the separation of the arsenic in the form of a mirror.

The following are the details and conditions for carrying out the test as recommended by the joint committee of the Society of Chemical Industry and the Society of Public Analysts.

The materials required are :—

1. *Hydrochloric acid.* The purest hydrochloric acid obtainable is very rarely free from arsenic. To the "pure" acid as purchased for analysis, diluted with distilled water to a sp. gr. of 1·10, sufficient bromine is added to colour it strongly yellow (about 5 c.c. per litre); sulphurous acid, either gaseous or in aqueous solution, is then added *in excess*, and the mixture allowed to stand for at least twelve hours; or hydrobromic acid and sulphurous acid may be used. The acid is then boiled till about one-fifth has evaporated, and the residue can either be used direct or it may be distilled; the whole of the arsenic is volatilised with the first portion.

2. *Sulphuric acid.* This is more frequently obtainable arsenic-free than hydrochloric acid. If not procurable, to about half a litre of sulphuric acid, "pure for analysis," a few grams of sodium chloride are added and the mixture distilled from a non-tubulated glass retort, the first portion of the distillate, about 50 c.c., being rejected. For the purpose of the test, one volume of the distilled acid is diluted with four volumes of water.

3. *Nitric acid* can, as a rule, be obtained free from arsenic, without much difficulty, the pure redistilled acid being used. This should be tested by evaporating 20 c.c. in a porcelain dish, which should then be washed out with dilute acid, and tested as described below.

The purified acids should be prepared as required, and should not be stored for any length of time. If this be unavoidable, however, Jena flasks are to be preferred, since most bottle glass is liable to communicate traces of arsenic.

4. *Zinc.* Arsenic-free zinc is obtainable from chemical dealers. It should be re-granulated by melting and pouring it from some height into cold water. A. H. Allen holds it to be essential, both for a regular evolution of hydrogen and for the formation of uniformly deposited brown-coloured mirrors, that the zinc should contain a trace of iron.

5. *Calcium hydroxide.* Even when made from white marble this is not always free from arsenic; a selection must, therefore, be made from various samples. If pure lime is not obtainable, magnesia may equally well be used, and can more readily be obtained of sufficient purity.

6. *Calcium chloride.* This salt often contains arsenic, and before being used as a drying agent must be freed from the volatilisable part of the

impurity by moistening it with strong hydrochloric acid, fusing, and regranulating.

The apparatus to be used is shown in Fig. 128.

A bottle or flask, *a*, holding about 200 c.c. (for frothing materials this should be preferably wider at the top than at the bottom) is fitted with a doubly bored cork, or rubber stopper, or with a ground-in glass connection carrying a tap funnel, *b*, holding about 50 c.c., and an exit tube, *c*. The latter is connected with a drying tube, *d*, containing first a roll of blotting-paper, *e*, soaked in lead acetate solution and dried, or a layer of cotton wool prepared in a similar way, then a wad of cotton wool, *f*, then a layer, *g*, of granulated calcium chloride, and finally a thick wad, *h*, of cotton wool. To this tube is fitted a hard glass tube, *i*, drawn out as shown in the figure to a thinner tube, *k*, and of such external diameter that at the place where the arsenic mirror is to be expected, the tube just passes through a No. 13 Birmingham wire gauge (corresponding with 0·092 inch = 2·34 mm.). The exact size is not material, but all tubes used for standards and tests should be as nearly as practicable of the same diameter. A good Bunsen flame is used to heat the hard glass tube close to the constriction. About one inch of tube, including the shoulder, ought to be red hot. A piece of moderately fine copper gauze,

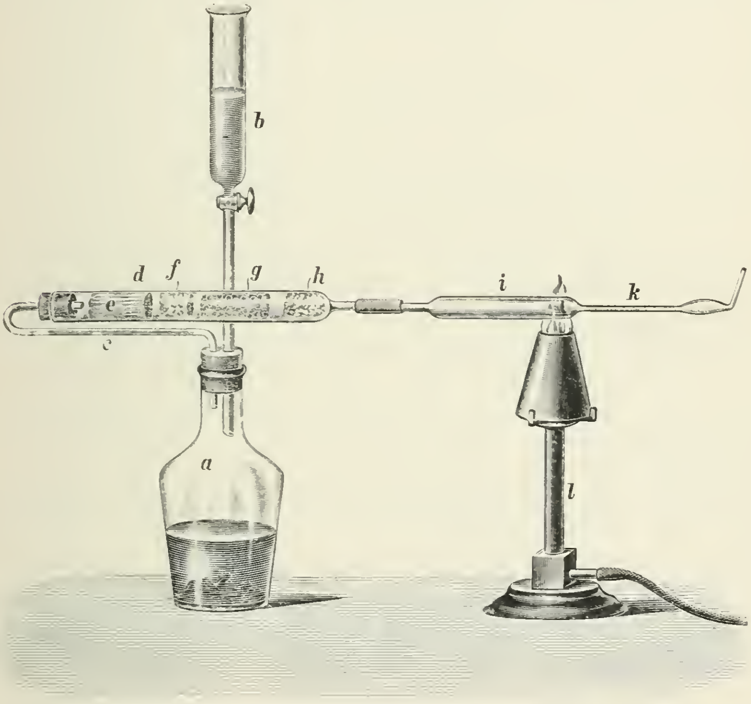

FIG. 128.

about one inch square, wrapped round the portion of the tube to be heated, assists in ensuring an equal distribution of heat.

Method of testing. About 20 g. of zinc are placed in the bottle, *a*, and washed with water to clean the surface, as particles of dust may contain arsenic; all the parts of the apparatus are connected up, and a sufficient quantity of acid, prepared as described, is allowed to flow from the funnel, *b*, so as to cause a fairly brisk evolution of hydrogen. When the hydrogen flame, which during the heating of the tube, *i*, should be kept at as uniform a height as possible (about a quarter of an inch), burns with a round, not pointed tip, all air has been removed from the apparatus. The plug in *d* prevents the flame from striking back. The burner is then placed under the hard glass tube as described, and more acid (10 to 20 c.c. is generally enough) run in as required. With good materials no trace of a mirror is obtained within half an hour. Great care must be taken that when additions of acid are made to the zinc, no air-bubbles are introduced, since in presence of air the arsenic mirror may become black and unevenly distributed; when the experiment is properly conducted the mirror is brown. Should the blank experiment not be satisfactory, it must be ascertained, by changing the materials methodically, whether the fault lies with the acid, zinc, or other materials, or with the apparatus.

Preparation of standard mirrors. When a satisfactory blank experiment has been obtained, a series of standard mirrors are prepared under the following conditions:—

A hydrochloric acid solution of arsenious oxide, containing 0·001 mg. As_2O_3 per c.c., is prepared by diluting a stronger solution with distilled water. Two c.c. of this solution, equal to 0·002 mg. of arsenious oxide, are introduced into the apparatus, a new tube, *ik*, having been joined to the drying tube. If the zinc is sensitive, a distinct brown mirror is obtained after twenty minutes. It is important to note that some "pure" zinc is, from a cause at present unknown, not sufficiently sensitive; that is to say, the addition of minute quantities of arsenic produces no mirror. The portion of the tube, *ik*, containing the mirror is sealed off while still filled with hydrogen; in contact with air the mirrors gradually fade. Mirrors are then similarly made with 0·004, 0·006, 0·008, and 0·01 mg. of arsenious oxide. With a little practice it is easy to obtain the deposits of arsenic neatly and equally distributed. The standard mirrors, properly marked, are mounted on a white card or porcelain slip. It is important to bear in mind that the first stage of every test must be a blank of at least twenty minutes.

Hydrochloric acid is somewhat more sensitive than sulphuric acid; that is to say, it gives rather denser mirrors with minute quantities of arsenic. If for any reason, sulphuric acid is preferred, the set of standard mirrors must be prepared with this acid.

Organic materials, such as beer, yeast, etc., cannot be tested, when sulphuric acid is used, without destruction of the organic matter, whilst, as a rule, they can be directly tested with hydrochloric acid. However, many materials are met with in which it is preferable to destroy the organic matter.

Procedure without destruction of organic matter. The apparatus is started and a blank experiment allowed to go on for twenty minutes. If no trace of a deposit is obtained, 10 c.c. of the liquid to be tested and 10 c.c. of hydrochloric acid are put into the funnel, *b*, and slowly introduced into the bottle, care being taken to exclude air-bubbles. Some materials, such as beers, are apt to froth, hence the necessity for the slow introduction of the sample. If after about ten minutes no mirror appears, another 10 c.c. of the liquid with 10 c.c. of hydrochloric acid are added, and the experiment continued for from fifteen to twenty minutes, acid being added from time to time as may appear necessary.

The report also deals with the special precautions to be observed in the examination of malt, hops, sugar, and other brewing materials, as well as the particulars for cases in which the organic matter present must be destroyed, as is frequently essential. Fuel, for example, is incinerated after mixing with lime or magnesia, and the resulting residue extracted with hydrochloric acid to obtain the "total arsenic."

If sulphites are present they must be oxidised by bromine, the excess of the latter being removed by heating.

The committee found that arsenic acid as well as arsenious acid can be detected and estimated by the procedure described. The quantitative results are, of course, only approximate, and cannot be relied upon for quantities of arsenious oxide below 0·003 mg. As an additional precaution, a second tube should always be substituted for that containing the mirror, and the experiment continued for a further period of from fifteen to twenty-five minutes, and any arsenic deposited added to that previously obtained. As a further check, the tests should always be made in duplicate.

To prove that the mirror obtained actually consists of arsenic, the narrow portion of the tube, which should not contain more arsenic than corresponds to 0·01 mg. As_2O_3, is cut off, the hydrogen displaced by air, and the ends of the tube then fused together. The sealed-up tube is then drawn several times through a Bunsen flame until the mirror has disappeared; on cooling, minute crystals of arsenious oxide appear. The sparkling of the crystals can be seen with the naked eye, if the tube be held in front of a luminous flame, and the crystals may be readily identified under the microscope.

By carrying out the test in the manner described, it is possible to detect, when working with 20 g. or 20 c.c. of substance, so low a percentage as 0·000015 As_2O_3 or one part As_2O_3 in 7,000,000.

The foregoing description is intended for the detection of extremely minute quantities of arsenic in food-stuffs and the like for forensic purposes; fuel is included on account of its use in the "kilning" of malt.

For the examination of sulphuric acid the method may be simplified by suitable modifications. For works purposes, for example, in testing whether, in purifying, all the arsenic has been precipitated by sulphuretted hydrogen, a much simpler apparatus will suffice, the test being frequently carried out in a flask fitted with a glass tube drawn out to a point and bent at right angles, and the examination made by observing whether the hydrogen flame will produce a stain on cold porcelain. If no stain is produced, it is assumed that only harmless traces of arsenic remain in the acid.

A further refinement in the method for the detection of arsenic has resulted from the work of the special Committee,[1] appointed by the Board of Inland Revenue, of which Prof. T. E. Thorpe acted as chairman. In the report two methods of carrying out the Marsh-Berzelius test are described, namely, the zinc method and the electrolytic method. The details for the first agree with those of the earlier arsenic committee (p. 364), except that the apparatus recommended is much smaller and the quantities of acid and zinc employed correspondingly less. The gas evolution takes place more slowly and the arsenic is deposited on a smaller surface of glass, which latter allows of a better comparison with the standard mirrors. These improvements are considered essential by the Inland Revenue Committee. Where cost of apparatus need not be considered and where electrical current of suitable strength is available, the evolution of hydrogen by electrolysis is recommended. The design of the apparatus and the manner of carrying out the test, as worked out in the Government Laboratory, are illustrated and minutely described in the report. In this method the conditions of experiment may be made absolutely uniform, and more exact comparisons with the standard mirrors should, in consequence, be obtained; further, all troubles arising from the presence of arsenic in the zinc are eliminated.

The apparatus, Fig. 129, consists of the following parts. The glass vessel A, open below, is fitted with a ground-in stopper furnished with a tap funnel the tube of which projects slightly below the stopper. The stopper is provided with a bent tube B′, to which the calcium chloride tube C is attached by a ground-glass connection. A strong platinum wire, *a*, is also fused into the stopper, and to it a conical-shaped

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[1] Report of the Committee appointed by the Commissioners of Inland Revenue to specify the ingredients of beers and the materials used in their preparation which are liable to be contaminated by arsenic, and to prescribe tests, etc.; published by Wyman & Sons, London, 1903. *Cf.* also, *J. Chem. Soc.*, 1903, **83**, 974.

platinum cathode, *a′*, pierced with several holes, is attached. The vessel A is supported by a porous cell D, the distance between the walls of the two vessels being from 2 to 3 mm. The porous cell is made of Pukall's porous porcelain, the walls of which are from 1 to 1·5 mm. thick; it stands in the thick-walled, glass anode vessel E. The anode consists of a strip of platinum foil, 2 cm. broad, coiled loosely round the cell D, and connected to the circuit by a strong platinum wire. The whole stands in a cooling-vessel, F, by aid of which the temperature is kept below 50°. The tube C contains firstly a plug of cotton wool, then for a length of 5 cm. pure, rather finely granulated, calcium chloride, which must be renewed after every three or four experiments, followed by a second plug of cotton wool, and finally a roll of lead acetate paper; this is prepared by soaking filter paper in a cold saturated solution of lead acetate, and after drying in the air, cutting it into strips 1 cm. wide and then rolling it into a coil so as to fit loosely in the tube. A further small spiral roll of lead paper is also inserted in the exit-tube from C, which is connected with the constricted glass tube G by means of a small piece of non-vulcanised rubber, care being taken that the ends of the glass tubes are in contact. The tube G is made from a piece of Jena glass tubing of 3·5 mm. internal and 5 mm. external diameter, and is cleaned by successive treatment with acid, alcohol, and water. It is then dried and heated in the blowpipe so that a portion of the tube, about 2 cm. in length and 5 cm. from the end, is softened, when it is drawn out to a length of 7 to 8 cm. and to a uniform external diameter of 2 mm. The tube is then cut off near the end of the narrowed

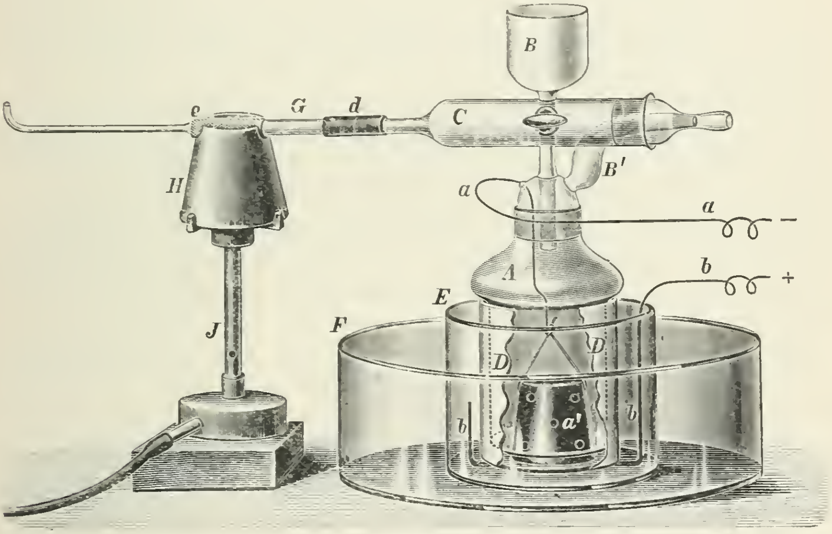

FIG. 129.

portion and the latter bent upwards to a height of 1 cm.; it is supported in slots in the metal cone H, surrounding the Bunsen flame; a piece of platinum gauze, *e*, about 2 cm. square, is wrapped round the portion of the tube to be heated in the burner. The small burner J has a circular base 12 mm. high and a tube 6 cm. high, and 5 mm. internal diameter.

The resistance of the apparatus is 1·4 ohms, and working at 7 volts potential difference between the pole wires and employing a current of 5 amperes, 40 c.c. of hydrogen are liberated per minute; this gives a steady flame 2 mm. high. The original description contains directions for arranging the apparatus so as to permit several tests being carried out simultaneously.

The sulphuric acid solution employed in the apparatus is prepared from pure sulphuric acid, tested especially for freedom from arsenic, which is diluted in the proportion of 7 vols. of water to 1 vol. of concentrated acid.

To apply the test to sulphuric acid, 5 c.c. of the sample are diluted with 20 c.c. of water, 0·5 g. potassium metabisulphite added, the solution boiled to drive off the sulphur dioxide, and allowed to cool. The object of the addition of the metabisulphite is to reduce any arsenic acid or arsenate present to the "arsenious" state, as this electrolytic method is only applicable to arsenic in the condition of an arsenite or of arsenious acid.

To carry out a test, the vessels A, B, and E are first thoroughly washed with water, cold water poured into the cooling vessel F, and the tube G connected with the drying tube C as described. The wires *a* and *b* are then connected with the current by means of binding screws, 30 c.c. of dilute sulphuric acid poured into the anode vessel E, and 20 c.c. into the porous cell D through the funnel B; the current is then switched on; after ten minutes the air will have been sufficiently displaced to allow the hydrogen to be lighted. At the same time the burner J is lighted, and the flame so adjusted that the platinum gauze *e* is maintained at a red heat. If at the end of a further fifteen minutes no brown ring has appeared in the narrow portion of the tube G, it is safe to assume that the acid is free from arsenic. If this be the case, 2 c.c. of rectified amyl alcohol are admitted to D through B, and followed immediately by the acid to be tested, which has previously been prepared as described above, and the funnel rinsed with 5 c.c. of water; the funnel tube is thus kept full of liquid, and so excludes air from the apparatus. The object of the addition of the amyl alcohol is to prevent frothing. If arsenic be present, a deposit will be formed, after a few minutes, at a point 1 to 2 cm. removed from the heated portion of the tube; after thirty minutes practically all the arsenic will in most cases have been deposited. The tap in B is then opened, the outer end of G immediately held with a pair of forceps, and a small pointed flame directed against the tube between the end and the deposit at a point 3 cm. from the latter. The tube fuses together immediately and is drawn off. The electric current is then switched off and the tube G heated and drawn out near its wider end, care being taken not to heat the arsenic mirror. The piece of tube about 4 cm. long so obtained and containing the arsenic mirror, is placed on a piece of white paper and compared with standard mirrors prepared from very small quantities of arsenic employed in the form of a solution of pure arsenious acid in hydrochloric acid, and diluted so that 1 c.c. contains 0·01 mg. As_2O_3.

In order to obviate the necessity of reducing arsenic acid and arsenates, Trotman[1] adds a few drops of zinc sulphate solution to the contents of the inner cell; this causes the hydrogen to be evolved in a state of supertension which suffices to reduce any "arsenic" arsenic present. The same object has been more satisfactorily attained by using cathodes of metals, such as lead and zinc, which have a considerably greater supertension than platinum. Sand and Hackford[2] recommend the use of lead electrodes, and have described a suitable apparatus for the electrolytic estimation of minute quantities of arsenic, whilst W. Thomson[3] recommends zinc electrodes; in both cases a complete reduction of "arsenic" arsenic is said to be effected. Chapman and Law[4] have shown that arsenite solutions are completely reduced in presence of sulphuric acid when cathodes of lead, tin, or of cadmium are used, but that with other metals, including iron, a large proportion of the arsenic is retained in the cell; arsenate solutions behave similarly, but in no case is the whole of the arsenic evolved as hydride.

Kühn and Saeger[5] have described a modified form of the Marsh test, which permits of a quantitative estimation of the arsenic. Ackroyd[6] states that only the brown and not the blue modification of the arsenic mirror is suitable for quantitative comparison; the former results in the case of organic liquids (glucose, beer, etc.), the latter from inorganic solutions. Only dilute solutions should be employed in testing, and for exact work fresh standards should be made each time.

Bertrand[7] has proposed the following method for the detection of $\frac{1}{1000}$ mg. arsenic or less. The acid used is warmed to from 30° to a maximum of 60°, the zinc added, and all air driven out of the apparatus by pure carbon dioxide; 1 to 2 drops of platinic chloride solution and 15 c.c. of dilute sulphuric acid (1 : 5) added, followed after an interval of ten minutes by the solution to be tested. The gas evolved is dried by passing through a plug of cotton wool previously heated to 120°, and

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[1] *J. Soc. Chem. Ind.*, 1904, **23**, 177.

[2] *J. Chem. Soc.*, 1904, **85**, 1018.

[3] *J. Soc. Chem. Ind.*, 1904, **23**, 799

[4] *Analyst*, 1906, **31**, 3.

[5] *Ber.*, 1890, **23**, 1798.

[6] *J. Soc. Chem. Ind.*, 1902, **21**, 1900.

[7] *Bull. Soc. Chim.*, 1902 [3], **27**, 851.

then through a carefully cleaned glass tube of 1 mm. diameter, which is narrowed by drawing out at a point some 10 to 15 cm. behind the place at which the ring is to be produced. A length of 20 cm. of the tube is heated to incipient redness. In the case of thick-walled tubes it is advisable to confine the heated space by means of strips of filter paper which are kept moist. Finally, the tube is sealed at both ends in a current of hydrogen. According to Treadwell,[1] the addition of platinic chloride is inadmissible. Pederson[2] gives similar details to those of Bertrand.

The zinc sometimes appears to be quite inactive (*cf.* p. 366), but such zinc has the peculiar property of becoming active on remelting and granulating. Allen ascribes this to the trace of iron, which may be taken up on melting in an iron ladle, and on this account he purposely adds a trace of ferric sulphate. Large quantities of iron are, however, to be avoided, since according to Parsons and Stewart[3] they cause a portion of the arsenic to be retained in the hydrogen generating flask. The influence of metallic salts on the sensitiveness of zinc has been especially studied by Chapman and Law.[4] Salts of palladium, platinum, nickel, and of cobalt prevent the reduction of arsenic to its hydride by zinc, whilst those of cadmium, tin, lead, aluminium, magnesium, and the alkali metals have no effect. Alloys of most metals with "sensitive" zinc, similarly inhibit the reduction, with the exception of the alloys of zinc with tin and with cadmium. If, however, 2 g. of cadmium sulphate, or of stannous chloride, or of lead acetate, be added to one of these insensitive alloys (with the exception of that with nickel), the whole of the arsenic is evolved as hydride. Similarly, the addition of 2 g. of cadmium sulphate renders insensitive zinc capable of reducing arsenic compounds; also, magnesium is rendered sensitive by the addition of a cadmium, zinc, or lead salt.

Arsenic-free zinc is readily prepared, according to Hehner,[5] by melting about 500 g. of zinc with about 1 g. of metallic sodium; on stirring, a black scum is formed on the surface of the metal, which is removed. The fused metal is then poured into a second crucible, again treated with sodium, and granulated. If this treatment is carefully carried out, the zinc obtained is absolutely free from arsenic.

The suggestion to employ aluminium foil and sodium hydroxide in place of zinc, cannot be recommended for exact work. According to Hehner,[6] it is possible, when working with aluminium and sodium hydroxide solution, to fail in obtaining a mirror even when 0·2 mg. of arsenious oxide is present in 25 c.c. of the solution.

Great differences of opinion exist as to the influence of sulphites,

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[1] *Analytical Chemistry*, vol. i., p. 191.

[2] *Chem. Centr.*, 1903, I., 250.

[3] *J. Amer. Chem. Soc.*, 1902, **24**, 1005.

[4] *Analyst*, 1906, **31**, 3.

[5] *J. Soc. Chem. Ind.*, 1902, **21**, 675.

[6] *Chem. News*, 1901, **83**, 34.

which are frequently present in the case of beer. According to some authorities they interfere with the formation of the arsenic mirror, and should consequently be oxidised with bromine water before testing (*cf.* p. 367), whilst others maintain that they exert no prejudicial effect. The extremely small amount of sulphur dioxide which may be present in sulphuric acid need scarcely be considered. The presence of sulphites only calls for consideration in the examination of beer, to which calcium bisulphite has been added to check fermentation; traces of sulphur dioxide may also arise from sulphuring casks or hops.

Allen[1] purifies the hydrochloric acid intended for use in the Marsh test by adding a slight excess of potassium permanganate, and distilling. The distilled acid is quite free from arsenic, but the first fraction coming over contains chlorine and must be rejected. Ling and Rendle[2] effect the purification by boiling hydrochloric acid of constant boiling-point, mixed with a small proportion of methyl alcohol, in a reflux apparatus, under reduced pressure, with bright electrolytic copper, free from arsenic; a little arsenic-free granulated zinc is added to the acid. The acid is then distilled over pure copper.

Other contributions concerning the estimation of minute quantities of arsenic have been made by Lockemann,[3] Mai and Hurt,[4] Bishop,[5] Bertrand and Vamossy,[6] and especially in the last report of the Analysis Committee of the International Congress of Applied Chemistry.[7]

That selenium affects the delicacy of the test, has been shown both by Dawydow[8] and by Berry.[9] In this connection Rosenheim and Tunnicliffe[10] have drawn attention to the fact that selenium, similarly to arsenic, may give rise to symptoms of poisoning.[11] Rosenheim states that the presence of selenium is not shown by the Marsh test, but that when present with arsenic it influences the size of the arsenic mirror, and may even, under certain conditions, entirely prevent its formation. The Reinsch test may be satisfactorily employed in presence of selenium, provided silver foil is used instead of copper. Further, the Gutzeit test is not influenced by the presence of selenium, though Bettendorf's test is. Schindelmeiser[12] has shown that in the Marsh test selenium, if present, is deposited on the zinc, and that after such deposition is complete arseniuretted hydrogen is evolved and may then be detected as usual.

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[1] *J. Soc. Chem. Ind.*, 1902, **21**, 903.

[2] *Analyst*, 1906, **31**, 37.

[3] *Z. angew. Chem.*, 1905, **18**, 416.

[4] *Z. anal. Chem.*, 1904, **43**, 537.

[5] *J. Amer. Chem., Soc.*, 1906, **28**, 178.

[6] *Chem. Centr.*, 1906, **I.**, 1461.

[7] *Report*, 1906, pp. 280-318.

[8] *Chem. Centr.*, 1895, **I.**, 811.

[9] *J. Soc. Chem. Ind.*, 1901, **20**, 322.

[10] *Ibid.*, 1901, **20**, 390.

[11] *Chem. News*, 1901, **83**, 280.

[12] *Chem. Centr.*, 1902, **II.**, 960.

B. Reinsch's Test.

This test depends on the fact that clean copper when immersed in a hydrochloric acid solution of arsenious acid becomes covered with a grey coating of copper arsenide As_2Cu_5; the deposit is formed in the cold if much arsenic is present, but only on warming if the solution be dilute. Arsenic acid only gives the reaction on warming. Since antimony also gives a coating of similar appearance, any deposit formed must be specially examined for arsenic (cf. *infra*).

The Reinsch test has now been discarded to a considerable extent, owing to its not being approximately quantitative in character, and also because it is not reliable when the arsenic is present as arsenic acid, or when sulphites are present. The test is, however, of considerable value in certain cases. According to Allen[1] it is preferable to other tests for detecting arsenic in beer, etc. To carry out the reaction he purifies the hydrochloric acid as described above (p. 364), adds a small quantity of the acid and bromine water to 100 c.c. of the beer, boils for a few minutes to oxidise any sulphite present, adds a small quantity of cuprous chloride to reduce the arsenic to the arsenious condition, immerses 1 sq. cm. of copper foil in the solution and boils for half an hour, adding water from time to time to replace that lost by evaporation. If the copper becomes darkened, it is dried on the water-bath, cut into strips, and examined for arsenic by heating one of the strips in a narrow test-tube, and observing whether a sublimate of the characteristic octahedra or tetrahedra of arsenious oxide is formed. Larger crystals are obtained by previously warming the upper portion of the subliming-tube, and the appearance of the crystals may be made more distinct by filling the tube with water. A similar procedure, together with a minute description of the various details involved in carrying out the test, has been published by a committee appointed by the Brewer's Central Association, Manchester;[2] the addition of an oxidising agent to destroy the sulphite and of a reducing agent to convert arsenate to arsenite, is omitted.

C. Gutzeit's Test.

This test is based on the action of arseniuretted hydrogen on solid silver nitrate or mercuric chloride, prepared by allowing a drop of the respective solution to dry on filter paper, or preferably, according to Eidenbenz, by dissolving a small crystal *in situ* on the paper, and drying. Silver nitrate is first turned yellow, owing to the formation of silver arsenide, and subsequently black, owing to separation of metallic silver; mercuric chloride is turned yellow owing to the formation of a

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[1] *J. Soc. Chem. Ind.*, 1901, **20**, 281.

[2] *Ibid.*, 1901, **20**, 646.

mercurous salt having the composition $As(HgCl)_3$. The test is generally performed by placing a small piece of granulated arsenic-free zinc in a test-tube, adding the material to be tested, and then, provided the material itself is not acid, a small quantity of dilute sulphuric acid. A plug of cotton wool is placed in the upper part of the tube and the tube capped with the previously prepared piece of filter paper. Sulphuretted hydrogen, phosphoretted hydrogen, and antimoniuretted hydrogen interfere with the reaction. The test is, however, frequently employed in the examination of commercial acids and of other substances; its applications and reliability have been specially studied by Flükiger,[1] Richardson,[2] Gotthelf,[3] Dunstan and Robinson,[4] and by Goode and Perkin.[5]

Kirkby's modification[6] of the Gutzeit test, which is frequently employed, is based on the observation that hydrogen sulphide may be completely removed from the evolved gases by means of a 5 per cent. solution of lead acetate, without any loss of arsenic. The apparatus used for carrying out the test is shown in Fig. 130. The hydrogen is evolved in the flask *a*, and is purified by passing through five bulbs, the two lower, *bb*, being half filled with 5 per cent. lead acetate solution, and the two upper, *cc*, with water. The purified gas passes into a small funnel, *d*, which is capped with the spotted and dried filter paper.

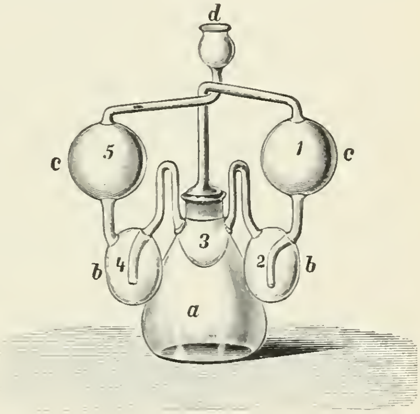

FIG. 130.

Tyrer[7] washes the gas with a 10 per cent. solution of lead acetate in a two-bulb apparatus of different type to the above. A simple form of apparatus, but perhaps not so reliable, has been described by Dowzard.[8]

F. W. Richardson[9] recommends the Gutzeit test, owing to its simplicity as compared with the Marsh test, and the possibility of carrying it out without special precautions.

Hehner[10] objects to the test on the ground that it is impossible to be certain that the stain obtained has been caused by arsenic, since hydrogen phosphide, etc., will also produce similar stains; apart from this, he considers the test very satisfactory and delicate. The

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[1] *Arch. Pharm.*, 1889, **27**, 1.

[2] *J. Soc. Chem. Ind.*, 1902, **21**, 901.

[3] *Ibid.*, 1903, **22**, 191.

[4] *Ibid.*, 1904, **23**, 999.

[5] *Ibid.*, 1906, **25**, 507.

[6] *Ibid.*, 1901, **20**, 281.

[7] *Ibid.*

[8] *Ibid.*, 1900, **19**, 1145.

[9] *Ibid.*, 1902, **21**, 902; *cf.* Gotthelf, *ibid.*, 1903, **22**, 191.

[10] *Ibid.*, 1901, **20**, 194.

method of testing proposed by Bird[1] overcomes Hehner's objection. The stain is treated with boiling hydrochloric acid, whereby a stain produced by phosphoretted hydrogen changes to lemon-yellow, one due to sulphuretted hydrogen disappears, one due to antimoniuretted hydrogen changes to pale grey, whilst that produced by arseniuretted hydrogen changes to brick-red, and may even be recognised when all the gases mentioned are present together in the test. The arsenic stain vanishes on treatment with bromine-hydrochloric acid, and the arsenic may be detected in the resulting solution by means of the brownish-red coloration produced on addition of stannous chloride.

The application of Gutzeit's test to the quantitative estimation of arsenic has recently been very fully investigated by Sanger and Black.[2]

D. Bettendorf's Test.

A few drops of the solution to be tested are added to 1 c.c. of concentrated hydrochloric acid, and $\frac{1}{2}$ c.c. of a solution of stannous chloride dissolved in an equal weight of strong hydrochloric acid added to the mixture. If arsenic be present the solution quickly turns brown, and a dark precipitate of metallic arsenic gradually separates out. The change occurs more readily on warming the solution. The reaction does not take place with aqueous solutions of arsenious acid, but only with the arsenious chloride which is formed from it in the presence of strong hydrochloric acid. Hydrogen phosphide and antimoniuretted hydrogen are not reduced by stannous chloride, and consequently do not interfere with the test.

According to Messel,[3] 0·01 mg. As_2O_3 in 1 c.c. sulphuric acid may be detected by this method.

The "tin foil test," which consists in the addition of strong hydrochloric acid to vitriol, then tin foil, and warming the solution, is practically identical with the Bettendorf test.

Of other tests that have been proposed, the following may be mentioned:—Donath[4] mixes 10 to 15 c.c. of the acid with an equal volume of water, adds a strongly acid solution of stannous chloride, heats nearly to boiling-point, and adds gradually a solution of sodium sulphite. Should arsenic be present, it separates out after some time in the form of finely divided yellow arsenious sulphide.

Seybel and Wikander[5] make use of the yellow precipitate AsI_3, produced on addition of potassium iodide. Free chlorine, ferric salts, nitrous acid, and lead interfere with this reaction.

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[1] *J. Soc. Chem. Ind.*, 1901, **20**, 390.

[2] *Ibid.*, 1907, **26**, 1115.

[3] *J. Soc. Chem. Ind.*, 1901, **20**, 192.

[4] *Z. anal. Chem.*, 1897, **36**, 664.

[5] *Chem. Zeit.*, 1902, **26**, 50.

QUANTITATIVE ESTIMATION OF SULPHURIC ACID AND OF ITS IMPURITIES

Free Sulphuric acid is estimated almost exclusively by titration with a standard solution of sodium hydroxide; the gravimetric determination by precipitation as barium sulphate is much less exact, and includes, moreover, any combined sulphuric acid which may be present. On the other hand, the volumetric method includes, as sulphuric acid, other acids which are present in the free state, but in commercial sulphuric acid the quantity of such other acids may be neglected as unimportant. In the case, however, of nitrating and of spent acids, the process described on p. 332 must be employed.

For the volumetric estimation, 2 to 3 g. of the acid are weighed off in a bulb pipette (Fig. 134); pipetting concentrated sulphuric acid is precluded by reason of its viscosity. The outside of the pipette is carefully cleaned, and the acid then allowed to flow into a relatively large volume of water, and the pipette re-weighed without washing out. The pipette need not be cleaned and dried for further determinations; it suffices to wash it out several times with the fresh acid to be tested.

Working with the quantity of acid given above, it is best to titrate with normal sodium hydroxide solution. The most satisfactory indicator is methyl orange, used sparingly (*cf.* p. 65), at the ordinary temperature and not in a warm solution. The amount of nitrous acid present in commercial vitriol does not interfere with the titration, but when larger quantities are present the test must be made as described on p. 66.

Sulphurous acid, if present in appreciable quantity, is best estimated by means of iodine (p. 116). Should nitrogen acids be present, sulphurous acid can only exist in traces, and cannot in such cases be determined quantitatively.

Nitrous acid (Nitrosyl-sulphuric acid), if present to any considerable extent, is estimated by potassium permanganate (p. 343). Such small amounts as cannot be determined with certainty either by permanganate or by the nitrometer, may be estimated colorimetrically. Of the various methods proposed for this purpose, that in which the modified Griess reagent (α-naphthylamine and sulphanilic acid) is used, is the best.[1]

Lunge and Lwoff found that a large excess of this reagent is necessary in order to obtain reliable colorimetric results, and that in the absence of such excess the intensity of the coloration increased at a much slower rate than corresponds to the percentage of nitrous acid present. Under suitable conditions and with at least one hundred times

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[1] Ilosvay, *Bull. Soc. Chem.*, 1894, **11**, 216; Lunge and Lwoff, *Z. angew Chem.*, 1894, **7**, 348; the whole of the literature relating to the subject is given in this paper.

the quantity of reagent theoretically necessary, the intensity of the coloration corresponds to the percentage of nitrous acid. By observing the details given below for the preparation of fresh reagent, the addition of 1 c.c. suffices in all cases to which the colorimetric method is applicable; the applicability is, of course, restricted to dilute solutions.

As is well known, the red coloration produced by the action of very minute traces of nitrous acid only appears after some time, and continues to grow in intensity for several hours. This might appear to be a drawback in the application of the test for colorimetric determinations, but it is not really so, for if all conditions, more particularly the time allowed for reaction, are equal, the colour intensity and percentage of nitrous acid remain comparable. If it be desired, therefore, to compare a solution of unknown strength with a known standard solution, it is only necessary to treat both with the reagent at the same time; the comparison may then be made either at the end of five minutes, or of half an hour, or after twenty-four hours, and always with the same result; for though the absolute colour intensity continually increases, the relative values remain the same.

In the case of aqueous solutions the comparison may generally be made directly, or at all events in a quarter of an hour, after the addition of the reagent. The presence of free mineral acid even in traces retards the reaction and renders the coloration less intense; a large amount of such acid entirely stops the reaction. This is due to the fact that the "coupling" of diazonium compounds is more or less inhibited by the presence of mineral acids. This difficulty is readily and completely overcome by adding sodium acetate in sufficient quantity to take up the whole of the mineral acid. The sodium acetate employed must, of course, give no coloration with the reagent, which is not always the case with commercial acetate. A "normal solution" for purposes of comparison must be prepared for the test. Dilute aqueous solutions of sodium nitrite or of nitrous acid are not suitable, owing to their instability. The nitrous acid is therefore employed in the form of the perfectly stable nitrosyl-sulphuric acid, and the "normal solution" is prepared by dissolving 0·0493 g. pure sodium nitrite (= 10 mg. N) in 100 c.c. of water and adding 10 c.c. of the solution to 90 c.c. of pure sulphuric acid; the solution thus contains 1/100 mg. of nitrite nitrogen per c.c.

In carrying out the test, 1 c.c. of the "reagent" diluted with about 40 c.c. of water is placed in each of two colorimeter cylinders; to the one is added 5 g. of solid sodium acetate and 1 c.c. of the "normal solution," to the other, 5 g. sodium acetate and 1 c.c. of the acid to be tested, and the whole well mixed so that the nitrous acid may react with the reagent at the moment of liberation. The colorations produced may be compared when desired; as a rule, five minutes' standing will prove sufficient. It is both unnecessary and disadvantageous to warm the solutions in this case. The solutions are best mixed by means of glass tubes blown below into a bulb corresponding to the inside diameter of the cylinders, as in the Nessler test for ammonia; by moving these stirrers up and down three or four times efficient mixing is secured.

The "reagent" is prepared by dissolving 0·100 g. pure white α-naphthylamine in 100 c.c. of water by boiling for one-quarter hour, adding to this solution 5 c.c. of glacial acetic acid, or the equivalent quantity of weaker acetic acid, followed by a solution of 1 g. of sulphanilic acid in 100 c.c. of water. The mixture must be kept in well-stoppered bottles. The solution readily discolours, but a faint rose coloration may be disregarded since it disappears when 1 c.c. of the reagent is diluted to the 50 c.c. used in the test; any stronger coloration may be removed by reducing the solution with zinc dust. One c.c. of the reagent will, after ten minutes, indicate distinctly the presence of 1/1000 mg. nitrite nitrogen in 100 c.c. of water.

Nitric acid.—For the quantitative colorimetric determination of nitric acid alone the brucine reaction may, according to Lunge and Lwoff, be employed, if the comparisons be made not with the initial red coloration but with the sulphur-yellow colour, which appears later. The solutions required are:—(1) a brucine solution prepared by dissolving 0·2 g. brucine in 100 c.c. of pure concentrated sulphuric acid; and (2) a normal solution of potassium nitrate containing $\frac{1}{100}$ mg. nitric acid nitrogen per c.c., prepared by dissolving 0·0722 g. of the pure salt in 100 c.c. of distilled water and making 10 c.c. of this stock solution up to 100 c.c. with pure concentrated sulphuric acid. These solutions are best kept in well-stoppered burettes fitted with glass taps; that intended for the "normal" solution should be graduated in $\frac{1}{20}$ c.c.

The sulphuric acid to be tested may be used directly, provided it is of not less than 1·7 sp. gr.; weaker solutions or acids must be mixed, in measured ratio, with pure concentrated sulphuric acid until the above strength is approximately attained (*cf.* p. 361); thus water alone will require the addition of three times its volume of concentrated acid.

Narrow 50 c.c. graduated cylinders of pure white glass are employed in comparing the colours; the graduated portion should be about 24 cm. in length, and the cylinder should extend a further 10 cm. beyond the last graduation mark, to allow for mixing. The Hehner cylinders, which are furnished with side taps at a height of about 5 cm. from the bottom, are very convenient. An actual colorimeter will, of course, give the most accurate results.

The test is made as follows:—1 c.c. of the normal solution and 1 c.c. of brucine solution are placed in one of the cylinders and pure concentrated sulphuric acid added up to the 50 c.c. mark; the mixture is then transferred to a flask and heated to 70° to 80°. When the colour has changed to sulphur yellow the solution is cooled and returned to the cylinder. The solution to be tested is treated similarly, it having been ascertained by a preliminary test whether the liquid should be used alone or after admixture with more concentrated sulphuric acid. Part of the solution is then poured away, or run off through the side tap, from one or other of the cylinders until the depth of colour is the same in each; the result is then obtained in the usual way by calculation from the measure of normal solution required per given volume of the unknown solution.

Selenious acid, according to Lunge,[1] has no effect on brucine.

In the presence of appreciable quantities of iron salts such as may occur, for example, in certain makes of concentrated sulphuric acid, the brucine test is less delicate, and the colour changes produced are not uniform even when equal quantities of nitric acid are present.

Lead.—Concentrated acids are diluted with an equal volume of water and twice the volume of alcohol, and allowed to stand for some time. The precipitated lead sulphate is filtered off, washed with dilute alcohol, dried, and ignited. The precipitate should be separated from the filter paper as completely as possible; the latter must not be ignited in a platinum crucible. 1 g. $PbSO_4 = 0{\cdot}6829$ g. Pb.

Iron.—If the quantity present is not too small, titration with permanganate may be employed after first reducing the iron to the ferrous state. This reduction may be carried out in many ways. The most general method is by means of chemically pure zinc, which should always be tested for freedom from iron, the reduction being hastened by warming, and carried out in a flask fitted with a Bunsen valve, or still better with a Contat bulb (Fig. 39, p. 106), or, according to Winkler, by wrapping a zinc rod with platinum wire. The reduction is complete when a drop of the solution, withdrawn by the aid of a capillary tube, produces no red coloration with potassium thiocyanate. The solution is allowed to cool, poured through a funnel provided with a platinum cone or nearly closed by a glass stopper (not through filter paper), to keep back the zinc, the flask and undissolved zinc washed with thoroughly boiled, air-free water, and the solution titrated. Should the zinc contain iron, a blank experiment must be made on at least 3 g. of the zinc, a weighed quantity of this taken for the reduction, and the operation continued until all the zinc has been dissolved.

Skrabal[2] employs about one hundred parts of zinc for each part of iron present, from which it will be seen that the smallest trace of iron in the zinc may lead to very appreciable error. Any titanic acid present will also be reduced by the zinc, and must consequently be taken into account.

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[1] *Ber.*, 1887, **20**, 2031.

[2] *Z. anal. Chem.*, 1903, **42**, 359.

For very small quantities of iron, Gintl[1] uses palladium charged with hydrogen, and so avoids introducing foreign matter into the solution. The hydrogenised palladium is prepared by electrolysing sulphuric acid with palladium as the cathode. Winkler[2] recommends a cylinder of palladium gauze for this purpose; this is suitable for reducing larger amounts of ferric salts.

Ebeling[3] proposes to add a little thiocyanate to the iron solution itself in order to ascertain when reduction is complete, the heating being continued until the red coloration has disappeared. Volhard[4] has shown that this is unsuitable, partly because the thiocyanate is destroyed in the process, and partly because traces of iron require a comparatively large excess of thiocyanate for their detection.

Other methods of reduction possess no advantages over the use of zinc for the estimation of small quantities of iron in commercial products, and are consequently seldom employed for this purpose. These include reduction by sulphuretted hydrogen recommended by Treadwell,[5] sulphurous acid, stannous chloride, etc. The case is, of course, different when large quantities of iron have to be determined, as for example in ores, when reducing agents other than zinc are frequently employed.

In the foregoing and analogous cases it is advisable to use *N*/20 potassium permanganate solution, prepared by diluting the seminormal solution (p. 99); 1 c.c. will correspond to the 0·002795 g. Fe. Further, a considerable quantity of the acid, say 50 c.c., should be employed for the test, since as a rule the quantity of iron present is only very small.

For very small amounts of iron the colorimetric ferric thiocyanate method may be employed. It is scarcely possible to obtain nitric acid absolutely free from iron for oxidising the iron in the solution to be tested to the ferric state, but this difficulty may be overcome by employing as pure an acid as possible, working only with small quantities, and by making a blank test for comparison. The best results are obtained under the following conditions worked out by Lunge.[6]

Glass-stoppered 25 c.c. cylinders of perfectly colourless glass, graduated in $\frac{1}{10}$ c.c. divisions, are employed in the test. The total height of each cylinder is 17 cm. and the internal diameter 13 mm.; to facilitate mixing, the graduated portion does not reach beyond a point 5 cm. below the stopper. The cylinders should be as similar in size as possible, so that equal volumes reach to the same height in each. At least three

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[1] *Z. angew. Chem.*, 1902, **15**, 398 and 424.

[2] *Massanalyse*, 3rd edition, p. 95.

[3] *Z. angew. Chem.*, 1901, **14**, 571.

[4] *Ibid.*, 1901, **14**, 609.

[5] *Analytical Chemistry*, vol. ii., p. 87. According to Cappadow (*Gaz. chim.*, **31** (ii.), 217) and Skrabal (*Z. anal. Chem.*, 1903, **42**, 359), this method is inexact, owing to iron sulphide being carried down with the precipitated sulphur.

[6] *Z. angew. Chem.*, 1896, **9**, 3.

cylinders are required; it is preferable to have four or six. The necessary reagents are: (1) a 10 per cent. solution of potassium thiocyanate; (2) pure ether; (3) a solution of ammonium iron alum prepared by dissolving 8·630 g. iron alum in a litre of water, and diluting 1 c.c. of this solution to 100 c.c.; the solution will thus contain 0·010 g. Fe per litre. This dilute solution soon decomposes, especially in the light, and can only be kept for a few days even in a dark place. The stronger solution, containing the 8·630 g. iron alum per litre, may be kept for a considerable time if protected from air and light; sometimes, however, it becomes cloudy even after a short time. The stability is increased by the addition of a little sulphuric acid, and if, in preparing the solution, 5 c.c. of pure concentrated sulphuric acid are added before filling to the litre mark, the solution will remain perfectly clear for a long period. The quantity of sulphuric acid thus introduced into the test scarcely amounts to 1 mg., and is therefore negligible. (4) Pure nitric acid as above.

Fifty c.c. of the diluted sulphuric acid are taken for the test and first oxidised by warming with exactly 1 c.c. of nitric acid. At the same time a second 1 c.c. of nitric acid (4) is diluted to 50 c.c. with distilled water. Should the experiment indicate later that the sulphuric acid solution should be still further diluted, the nitric acid solution must also be diluted to the same extent, so that in both cases the amount of iron introduced with the nitric acid will be the same. Any nitric acid which produces more than a very faint reddish tinge with the thiocyanate solution must be rejected.

Exactly 5 c.c. of the prepared solution of the sulphuric acid to be tested are then placed in one of the stoppered cylinders (A), and 5 c.c. of the diluted nitric acid in a second cylinder (B). To the latter a suitable quantity, say 1 c.c. of the iron alum solution, is then added from a burette, and to A an equal volume of water, so that the solutions in the two cylinders are brought to the same dilution. Five c.c. of the thiocyanate solution are next added to each solution. Both mixtures will redden, but the coloration is frequently of a somewhat dirty yellowish red, and its intensity bears no relationship to the iron content of the solution. Finally, 10 c.c. of ether are added to each cylinder and the contents thoroughly agitated. The aqueous solution contains a double thiocyanate of potassium and iron. This double salt is split up on shaking with ether, which dissolves only or preferably the iron thiocyanate, as is evidenced by the rose-red coloration of the ethereal solution as compared with the yellowish red of the aqueous solution. Shaking must be continued until the aqueous layer becomes colourless. The ethereal solution gradually darkens in colour, presumably owing to a further splitting up of the double thiocyanate; the solutions should therefore be prepared in rapid sequence, and preferably only compared after standing for several hours.

Differences of considerable magnitude are detected immediately, so that it only becomes necessary to employ, in addition to the cylinder A, containing the sulphuric acid solution, two other cylinders, B and C, to which have been added the approximately correct quantities of iron alum solution; the final comparison, however, is, as stated, not made for some hours. The solutions should not be allowed to stand too long, for instance, over night, for it sometimes happens that after long standing the ether becomes nearly, or even perfectly, colourless, only a strongly coloured narrow zone of liquid remaining at the dividing line between the ether and the water. This only occurs occasionally, and is to be attributed to traces of impurities, which are, however, present in such extremely small quantities that they cannot be identified.

The degree of accuracy of the method may readily be brought to ±0·1 c.c. iron alum solution, that is, to ±0·000001 g. Fe, on the 5 c.c. of solution taken, provided the volume of alum solution used does not exceed 2 c.c., equivalent to 0·000002 g. Fe. That is, the reading may be made to 1/20 of the total iron present; this may be looked upon as satisfactory, where only thousandths or hundredths of a per cent. come into account. It is not, however, sufficient for appreciably greater amounts, and for such the volumetric method must be employed.

The above degree of accuracy may be attained without difficulty by merely examining the ethereal layer by transmitted light. The comparison may be made more accurate by looking through the ethereal layer obliquely from above, or by holding the cylinders a little above a white surface, and looking through the full depth of liquid in the cylinder. This plan is much better than allowing the cylinders to stand on the white surface. Colorimeters, as ordinarily constructed, are not suited for this particular determination, no provision being made for shaking, preventing loss of ether, etc. Seyda[1] has described a method differing but little from the above, and intended for use in the examination of water.

Hydrochloric acid.—Ten c.c. of the acid are boiled in a small flask and the vapours evolved conducted to a surface of water contained in a second flask. The hydrochloric acid is dissolved by the water, and may be estimated by titration with alkali or with $N/10$ silver nitrate solution.

Arsenic.—About 20 g. of the acid are diluted with water, the solution filtered from any precipitated lead sulphate, and then treated with a current of sulphurous anhydride until the solution smells strongly of the gas, to reduce all arsenic compounds to the arsenious condition. Prolonged action, and a considerable excess of sulphur dioxide are necessary for the reduction. The excess of sulphur dioxide is removed by heating, aided by a current of carbon dioxide, the

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[1] *Chem. Zeit.*, 1898, **22**, 1086.

solution exactly neutralised by addition of sodium carbonate and bicarbonate, and titrated with $N/10$ iodine and starch solution till the colour-change to blue occurs. One c.c. of the iodine solution corresponds to 0·00495 g. As_2O_3. Iron must first be removed should it be present in appreciable quantity.

The presence of lead, antimony, copper, platinum, etc., somewhat complicates the determination.[1]

According to Böckmann, the reduced solution, freed from excess of sulphur dioxide as above, is treated for some hours at a moderate temperature with a current of sulphuretted hydrogen, which precipitates the arsenic and other metals which yield sulphides insoluble in acid solution. The precipitate is filtered off and well washed, at first with water rendered slightly acid with hydrochloric acid, and then with hot water until the washings leave no residue when evaporated on platinum foil. The precipitate, which contains arsenic sulphide and antimony sulphide, is dried and weighed. It is then moistened with cold water and, when thoroughly damped, extracted with dilute ammonia. The residue remaining on the filter, consisting of sulphur and antimony sulphide, is washed with hot water, dried, and weighed as above. The difference between the two weights gives the content of arsenic sulphide sufficiently accurately for technical purposes.

Neher[2] precipitates the arsenic in acid solution by sulphuretted hydrogen. Hattensaur[3] dilutes 500 c.c. of sulphuric acid with 500 c.c. of water, adds 500 c.c of dilute hydrochloric acid (1 : 2) to the solution, cooling during the addition, and passes sulphuretted hydrogen for three-quarters to one hour through the continually cooled solution, finally filtering off the precipitate, which consists of pure As_2S_5 free from lead. The filtration may be performed in a platinum or porcelain Gooch crucible (p. 26); any trace of sulphur is removed by a final washing with hot alcohol, and the precipitate weighed in the crucible. In the absence of a Gooch crucible, the precipitate may be dissolved on the filter in 20 c.c. of dilute ammonia (1 : 2), the solution evaporated in a porcelain crucible, the residue oxidised to arsenic acid, and estimated as magnesium ammonium arsenate. If the arsenic is weighed as pentasulphide, the determination can be made in from three to four hours.

Very minute quantities of arsenic are estimated approximately by comparison of the arsenic mirrors made according to the Marsh-Berzelius test (*cf.* p. 363 *et seq.*).

Atterberg[4] estimates arsenic colorimetrically by boiling with strong hydrochloric acid, collecting the distillate in water, evaporating this with nitric acid, and finally reducing by stannous chloride or sodium hypophosphite.

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[1] L. M'Cay, *J. Amer. Chem. Soc.*, 1885, **7**, 6.

[2] *Z. anal. Chem.*, 1893, **32**, 45.

[3] *Z. angew. Chem.*, 1896, **9**, 130.

[4] *Chem. Zeit.*, 1901, **25**, 264.

Fuming Sulphuric Acid (Anhydride, Oleum)

Fuming sulphuric acid is generally regarded as a solution of sulphur trioxide (sulphuric anhydride, SO_3) in sulphuric acid monohydrate (H_2SO_4). As a matter of fact, the chief constituent is generally pyrosulphuric acid ($H_2S_2O_7$), and the so-called 45 per cent. oleum consists entirely of this. The other varieties below 45 per cent. are mixtures of pyrosulphuric acid with monohydrate, and those above 45 per cent. mixtures of pyrosulphuric acid with anhydride. The strength is always given as percentage of anhydride, no account being taken of the presence of pyrosulphuric acid. The latter is looked upon, from the analytical standpoint, as a mixture of fifty-five parts H_2SO_4 with forty-five parts SO_3.

Properties of fuming sulphuric acid. Pyrosulphuric acid, $H_2S_2O_7$, that is oleum of 45 per cent. SO_3, as well as those acids which contain in addition to the pyrosulphuric acid only little H_2SO_4 or SO_3, that is acids from slightly below 40 per cent. up to nearly 60 per cent. SO_3, are solid; on the other hand, the varieties ranging from 0 to nearly 40 per cent., and from 60 per cent. to 70 per cent. SO_3, are oily liquids. From 70 per cent. onwards the oleum is once more solid, until it finally passes to pure anhydride.

Melting Points of Oleum. Knietsch.[1]

Per cent. SO_3.	Melting-Point.	Per cent. SO_3.	Melting-Point.	Per cent. SO_3.	Melting-Point.
0	+10	35	+26·0	70	+ 9·0
5	+ 3·5	40	+33·8	75	+17·2
10	− 4·8	45	+34·8	80	+20·0
15	−11·2	50	+28·5	85	+33·0 (27·0)[1]
20	−11·0	55	+18·4	90	+34·0 (27·7)
25	− 0·6	60	+ 0·7	95	+36·0 (26·0)
30	+15·2	65	+ 0·8	100	+40·0 (17·7)

Boiling Points of Oleum. Knietsch.[2]

SO_3, Total, per cent.	SO_3, Free, per cent.	Boiling-Point.	Barometric Pressure, Mm.
82·3	3·64	212	759
83·4	9·63	170	759
86·45	26·23	125	759
89·5	42·84	92	759
93·24	63·20	60	759
99·5	97·2	43	759

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[1] *Ber.*, 1901, 34, 4100. The figures in brackets are the melting points of the fresh non-polymerised acids.

[2] *Ibid.*, 4110.

Specific Gravity of Fuming Sulphuric Acid at 35° C.
Knietsch.[1]

Total SO_3 per cent.	Free SO_3 per cent.	Specific Gravity.	Total SO_3 per cent.	Free SO_3 per cent.	Specific Gravity.
81·63	0	1·8186	91·18	52	1·9749
81·99	2	1·8270	91·55	54	1·9760
82·36	4	1·8360	91·91	56	1·9772
82·73	6	1·8425	92·28	58	1·9754
83·09	8	1·8498	92·65	60	1·9738
83·46	10	1·8565	93·02	62	1·9709
83·82	12	1·8627	93·38	64	1·9672
84·20	14	1·8692	93·75	66	1·9636
84·56	16	1·8756	94·11	68	1·9600
84·92	18	1·8830	94·48	70	1·9564
85·30	20	1·8919	94·85	72	1·9502
85·66	22	1·9020	95·21	74	1·9442
86·03	24	1·9092	95·58	76	1·9379
86·40	26	1·9158	95·95	78	1·9315
86·76	28	1·9220	96·32	80	1·9251
87·14	30	1·9280	96·69	82	1·9183
87·50	32	1·9338	97·05	84	1·9115
87·87	34	1·9405	97·42	86	1·9046
88·24	36	1·9474	97·78	88	1·8980
88·60	38	1·9534	98·16	90	1·8888
88·97	40	1·9584	98·53	92	1·8800
89·33	42	1·9612	98·90	94	1·8712
89·70	44	1·9643	99·26	96	1·8605
90·07	46	1·9672	99·63	98	1·8488
90·44	48	1·9702	100·00	100	1·8370
90·81	50	1·9733	...	...	...

This table may be used in calculating the quantity of concentrated sulphuric acid to be added to an oleum to obtain an oil of any desired lower strength in free SO_3. Gerster[2] gives the following formula for this purpose:—

$$x = 100 \frac{b - a}{a - c}$$

where x represents the quantity of sulphuric acid to be added to 100 parts of the oleum, a the total SO_3 per 100 parts of the acid desired, b the total SO_3 per 100 parts of the original strong oleum, and c the SO_3 per 100 parts of the acid used for dilution. The values for a and b are taken from the table; c is obtained by multiplying the percentage of H_2SO_4 present in the acid used for dilution by 0·816.

Impurities. These may be the same as those present in ordinary sulphuric acid, but since fuming acid is now made exclusively by the contact process, they will only occur in inconsiderable quantity. The examination for these impurities is carried out exactly as in the case of ordinary sulphuric acid (p. 377 *et seq.*).

[1] *Ber.*, 1901, **34**, 4101.

[2] *Chem. Zeit.*, 1887, **11**, 3.

Quantitative Analysis of Fuming Sulphuric Acid

The sampling of oleum is a matter of some difficulty. In the case of liquid oleum, or in that of the partially or completely crystalline products up to 45 per cent. SO_3, the difficulty is not very great, since the latter acids may be liquefied without danger by warming to 30° in closed vessels on the sand-bath. In works the soldered leaden vessels containing the acid are usually stored in a warmed room, so that the contents are always liquid. It is advisable to remove the stopper or other seal before warming, and to substitute a watch-glass; this does not cause any appreciable loss of SO_3, and checks the development of pressure, which might easily lead to an accident on removing the stopper.

Products rich in SO_3 cannot be completely liquefied by warming. A jelly-like residue always remains, but as this possesses the same composition as the liquefied portion, the sample may be drawn from the latter.

The portion for analysis is taken from these larger samples.

Solid oleum (pyrosulphuric acid) must be liquefied in the sample bottle by gently warming, before being withdrawn by the pipette for analysis; it will then remain liquid sufficiently long to allow of its flowing from the pipette even after weighing. Actual anhydride and oleum approaching this strength cannot be handled in this manner, as they fume too much. In such cases Stroof's method may be followed. This consists in weighing several portions of the anhydride in a glass-stoppered bottle, and then adding a weighed quantity of accurately analysed monohydrate sufficient to produce an oleum of about 70 per cent., which is liquid at the ordinary temperature. Solution is hastened by warming to 30° to 40°, with the stopper placed loosely in the bottle. The analysis of the mixture is then carried out in the ordinary way.

The value of an oleum depends chiefly on the content of free anhydride, SO_3; the results are accordingly calculated in the following manner. First, the total acidity is determined by titration and calculated to SO_3; the difference between 100 and the percentage so obtained is regarded as water, for each 18·1 parts of which 80·06 parts SO_3 are necessary for the formation of H_2SO_4; after all water has been allowed for in this way, any SO_3 remaining is taken as free anhydride. It must not, however, be forgotten that other substances

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[1] *Cf.* Fürstenau, *Chem Zeit.*, 1880, **4**, 18; Möller, *ibid.*, 1880, **4**, 569; Becker, *ibid.*, 1880, **4**, 600; Winkler, *Chem. Ind.*, 1880, **3**, 194; Clar and Gaier, *ibid.*, 1881, **4**, 251; Rosenlecher, *Z. anal. Chem.*, 1898, **37**, 209; Setlik, *Chem. Zeit.*, 1889, **13**, 1670; Rabe, *Chem. Zeit.*, 1901, **15**, 345; *Sulphuric Acid and Alkali*, **1**, p. 238.

may be present in addition to the water, especially sulphurous acid, SO_2. which, as will subsequently be seen, considerably affects the result, Solid constituents, in more than traces, are also occasionally present; these must be estimated and the percentages obtained deducted from the water value, otherwise the result obtained for the percentage of free SO_3 will be too low.

The analysis of fuming sulphuric acid or anhydride is carried out as follows:—

The oleum is weighed off in tared, thin-walled bulb tubes of about 20 mm. diameter, drawn out at both ends to form long capillaries. Three to 5 g. of the melted, completely homogeneous oleum, which is sufficient to nearly half-fill the tube, are drawn in by the following device. An ordinary narrow-necked flask is fitted with a rubber stopper, through which passes a well-ground glass tap provided with a piece of rubber tubing at its free end. A partial vacuum is produced in the flask by suction (with the mouth), the tap closed, the rubber tube passed over one of the capillaries of the weighing bulb, and the other capillary immersed in the oleum; on opening the tap the desired quantity of oleum is drawn into the bulb.

The bulb is then cleaned, one of the capillary ends sealed by fusion, and the whole weighed. Loss of anhydride by evaporation or by absorption of moisture through the non-sealed, capillary end does not occur to any appreciable extent during the weighing. In weighing, it is advisable to support the capillary ends of the bulb-tube on a small platinum crucible with two notches cut in the rim; this will prevent damage to the balance should breakage occur.

The weighed bulb is then placed in a small Erlenmeyer flask (Fig. 131), so that the bulb closes the neck and the point of the open capillary dips rather deeply into the water contained in the flask. By this means any loss of anhydride by evaporation is excluded. The point of the upper capillary is then broken, and after all the oleum has run out the tube is washed by dropping water through the upper capillary, and finally by sucking in water several times so as to completely fill the bulb. The solution is diluted to 500 c.c. and 50 c.c. taken for titration. The titration is made with $N/5$ sodium hydroxide solution (1 c.c. = 0·008 g. SO_3), using methyl orange as indicator (not litmus, *cf.* p. 391). Sulphurous acid is determined by titrating a second portion of the solution with iodine solution, and the quantity found deducted from the total acidity, as found in the titration with alkali.

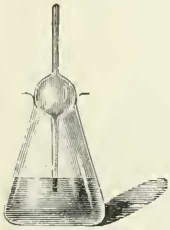
Fig. 131.

Clar and Gaier weigh the anhydride (oleum) in a glass bottle (Fig. 132), 58 mm. high and 17 mm. wide, fitted with a long, ground-in glass stopper broadened out to a bulb above the neck of the flask, and pierced on the top with a small hole which can be closed by a small glass stopper. The interior of the stopper is filled with glass wool moistened slightly with water. Two to 3 g. of the melted anhydride or fuming acid are introduced into the bottle, the stopper quickly inserted, and the whole weighed. The head of the stopper is then weighted by wrapping a strong platinum wire round the neck, and the bottle allowed to slide, mouth downwards, into a suitable flask of about 2 litres capacity placed in an inclined position, and containing about 500 c.c. of water at 50° to 60°. The flask is next placed in an upright position and covered with a watch-glass. It is advisable to bind the stopper to the bottle with thin platinum wire, to prevent its falling out.

Fig. 132.

With suitable weighting the bottle takes up an oblique position in the water, the head being directed downwards, which is the best position for the subsequent operation. At first the warmth of the water expands the air in the bottle and causes some acid to escape; later on, water is drawn in and dilutes the contents of the bottle without producing too violent a reaction. The dilution may be hastened by cooling the flask, but shaking or other violent movement must be avoided. Finally, the bottle is washed inside and out with water, the cooled solution made up to 1 litre, and 100 c.c. titrated with $N/5$ alkali as above.

Fig. 133.

A very convenient apparatus for weighing fuming sulphuric acid or melted anhydride is the glass tap-tube recommended by Winkler (Fig. 133).

The conically narrowed portion ending in a capillary must be absolutely uniform, and the tap, which may not be greased, should fit perfectly. The longer portion of the tube is one-half, or at most two-thirds, filled by suction with the acid to be examined, the tap closed, and the tube then inverted so that the acid runs down to the tap. The end of the tube is carefully cleaned with paper, and the tube and contents weighed in a horizontal position. No alteration in weight during weighing need be feared. The tube is then placed with the point downwards in a beaker containing water and the acid allowed to enter the water very gradually, the rate of the flow being best regulated by means of a screw clip. In the case of very strong acids or of pure anhydride which will remain liquid for a considerable time, dilution is effected by allowing the acid to escape on to a layer of coarsely powdered, crystallised, and perfectly neutral Glauber's salt. In this way dilution takes place quietly and without danger, on account of the water of crystallisation present in the salt. Finally, a few drops of water are allowed to enter the weighing-tube from above, and after standing for a short time the tube is thoroughly washed out. The Glauber's salt is dissolved in water, the solution made up to a known volume, and an aliquot portion titrated. This plan does not, however, give quite accurate results, as the colour change of the indicator (methyl orange) is less sharp in presence of the Glauber's salt.

The most convenient form of weighing apparatus, not only for oleum but also for other liquids, such as fuming acids of all kinds, ammonia, etc., which must be weighed out of contact with air, is the bulb-tap pipette designed by Lunge and Rey (Fig. 134).

FIG. 134.

The taps *a* and *c* must fit perfectly without grease. To fill the pipette the tap *c* is closed, *a* opened and, whilst applying suction at *d*, closed so that a partial vacuum is obtained in the bulb *b*. The point *e* of the tube is then placed in the acid, and *c* opened, whereby the acid rises in the pipette. Care must be taken that it does not reach the tap *c*; all vapours are retained in *b*. The tap *c* is then closed, the end of the tube *e* cleaned, and after returning the pipette to the protecting tube *f*, the whole is weighed. In the case of strongly fuming nitric acid and similar liquids a drop of the liquid may escape from the point *e* during the weighing; in such cases it is advisable to place a little water in the tube *f*, taking care, however, not to insert the empty pipette before the final weighing, lest its point become wetted. The pipette is then removed from *f*, the point *e* dipped into water, and the contents allowed to escape gradually by opening the tap *c*; a little water is admitted to *b* through *d* and *a*, and the whole finally washed after allowing to stand for some time. If only 0·5 to 1 g. of acid have been weighed off, the whole of the resulting solution is titrated, the result obtained being more accurate in this case than by diluting to a large volume and only titrating a portion. For larger quantities of acid the solution must be diluted to a measured volume and an aliquot part titrated.

The strongest oleum (over 70 per cent.) cannot be run into water directly without undergoing loss. Such acid is weighed in the bulb-tubes described above, both capillary ends fused, and the bulb placed in a flask containing a fairly large volume of water. The flask is then closed with a glass stopper, the bulb broken by shaking the flask, and after standing for some time the whole is titrated.

As already stated (p. 388), a deduction must always be made for sulphurous acid, which is seldom absent from commercial oleum. The sulphurous acid is generally estimated by titration with iodine and the quantity found deducted from the total acidity. Lunge[1] has pointed out that an error may easily occur in the latter titration, unless due attention be paid to the indicator employed and the stage at which the change of colour takes place; great differences exist between the various indicators in this respect. Thus with phenolphthalein the change occurs when 1 mol. SO_2 has combined with 2 mol. NaOH, that is, when Na_2SO_3 has been formed; with methyl orange, on the other hand, the change takes place when only 1 mol. NaOH has been added for 1 mol. SO_2, that is, as soon as $NaHSO_3$ has been produced. Litmus cannot be employed, since the results obtained are quite indefinite, lying between the limits given above (*cf.* p. 70).

It is thus inadmissible to employ litmus in titrating fuming sulphuric acid, since it will not show what allowance is to be made for the sulphurous acid; nor is phenolphthalein a good indicator in this case, owing to the unavoidable presence of carbonate in the sodium hydroxide solution. Ammonia is unsuitable for the titration. Methyl orange should therefore be used, bearing in mind that 1 c.c. normal sodium hydroxide solution (0·04006 g. NaOH) is neutralised by $\frac{1}{2}$ mol. SO_3 (0·04003 g. SO_3), but by a full molecule of SO_2 (0·06405 g. SO_2). Consequently for each 1 c.c. $N/10$ iodine solution required for the titration of the latter only 0·05 c.c. normal alkali solution must be allowed, and not the equivalent ratio 0·1 c.c. If this point be neglected very considerable error may result, since everything other than SO_2 and SO_3 is assumed to be water; thus an incorrect allowance for sulphur dioxide will not only show too little trioxide, but also a corresponding quantity of water in excess of the real value, and since the latter has to be credited with its corresponding amount of SO_3 (=4·443 times the quantity of water), the percentage of free trioxide may come out very much too low.

In an actual case the incorrect allowance for SO_2 led to an error of $8\frac{1}{4}$ per cent. in the free SO_3. This is, however, an extreme instance.

If the proportion of free trioxide is calculated by means of the table (p. 394), instead of by multiplying the water by 4·443, due allowance must similarly be made for the content of sulphur dioxide. Thus, taking the actual case just referred to, analysis proved the acid to contain 95·21 per cent. SO_3, 2·43 per cent. SO_2, and 2·36 per cent. H_2O. In using the table the SO_2 must be left out of account, that is, the SO_3 and H_2O are the only factors to be considered. It will not do to merely take from the table the value corresponding to a total percentage of 95·21 SO_3; this would only give 73·95 per cent. free SO_3,

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[1] *Z. angew. Chem.*, 1895, **8**, 22.

an even more incorrect result than the above. The correct procedure is to add the 2·36 parts H_2O to the 95·21 parts SO_3, giving in all 97·57 parts of acid and water with a percentage content of 97·58 SO_3. According to the table, it is found by interpolation that such acid corresponds to 86·80 per cent. free SO_3 and 12·20 per cent. H_2SO_4. This 86·80 per cent. must then be recalculated to the original acid, and so allow for the contained SO_2, giving $\frac{97{\cdot}57 \times 86{\cdot}80}{100} = 84{\cdot}69$ per cent. free SO_3 as the final value. The result obtained thus involves considerably more calculation than multiplying the percentage of water by its equivalent of sulphur trioxide; it is only fair to state, however, that this example does not lend itself particularly well to the table, which is drawn up for mixtures of anhydride and water only.

In the foregoing instance, as in all methods hitherto published for determining the strength of oleum, everything other than SO_2 and SO_3 is regarded as water. It is, however, advisable to estimate the *fixed impurities* by evaporation, since otherwise their weight multiplied by 4·443 is erroneously deducted from the free SO_3.

Rosenlecher[1] has described the method employed at Freiberg which is used for checking the process in the works. Weighing-tubes of the dimensions shown in Fig. 135 are made from glass tubing of 5 to 6 mm. diameter, a number of which are prepared at one time. The ends of the capillaries are narrowed to $\frac{1}{2}$ mm., and for strong oleum or anhydride to $\frac{1}{4}$ mm. The bulbs are filled by suction applied by the mouth through a capillary rubber tube fixed to the shorter capillary, a test-tube filled with soda crystals being interposed when necessary. Suction is applied until the liquid begins to rise in the bulb, and is stopped before the heavy anhydride vapours reach the shorter limb. The bulb is then turned so that the limbs point upwards, and the bulk of the liquid brought into the bulb by gentle tapping. Each bulb is carefully wiped with filter paper and supported opposite a corresponding number in a notched cardboard box. In weighing, the bulb is placed on a platinum crucible (p. 388), or held in a suitable brass wire support. If the above dimensions of the capillaries are adhered to, there is no danger of moisture being absorbed or of loss by evaporation, even in

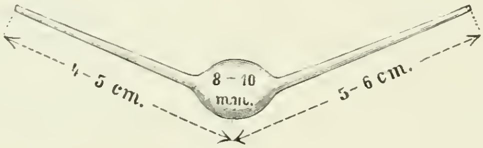

FIG. 135.

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[1] *Z. anal. Chem.*, 1898, **37**, 209.

the case of pure anhydride. Care must, however, be taken not to warm the bulbs in handling, either before or after weighing. To bring the acid into solution the bulb is placed in a bottle containing the indicator and 20 to 30 c.c. of water, at the temperature of the room. The previously wetted glass stopper of the bottle is then inserted, the bottle held in a horizontal position (the colour of the indicator should remain unchanged up to this time), the stopper securely fixed, and the bottle well shaken until the tube has been completely shattered and all white vapours have disappeared. The solution is then titrated in the bottle itself. The differences in the results obtained seldom exceed 0·15 per cent. even with rapid working. (This statement apparently relates to the total acidity and not to the free anhydride.)

Dobriner and Schranz[1] dissolve 6 to 8 g. of the oleum contained in a sealed tube by breaking the tube in a stoppered litre flask containing about 150 c.c. of water, and adding a weighed quantity of chemically pure dry sodium carbonate, so that only 3 to 4 c.c. of normal solution are required for titrating back. By this means errors in the standard solution, and in the burette, etc., are reduced to a minimum.

The results of the titration are first calculated to percentage of total SO_3 (combined and uncombined with water), each 1 c.c. normal sodium hydroxide solution corresponding to 0·04003 g. SO_3; the ratio between free SO_3 and the H_2SO_4 present may then be taken from the following table drawn up by Knietsch.[2] Or the general formula,

$$SO_3 = S - 4.443\,(100 - S),$$

may be employed, in which SO_3 stands for the free sulphur trioxide and S for the percentage total SO_3, as found by titration.

Grünhut[3] gives the following table (p. 395), which allows the percentage to be read directly to the hundredth part. The left-hand portion shows the amount of trioxide corresponding to the total percentage of H_2SO_4 as found. For 106 per cent. H_2SO_4, for example, the point of intersection of the vertical column 10 and the horizontal row 6 gives the desired percentage 26·657. The right-hand portion contains the values for the decimal places. The first decimal is found in the vertical column marked by the asterisk, and the horizontal line lying to the right is then followed until the column having the second decimal place for its heading is reached. Thus for 0·78 per cent. H_2SO the value is 3·465. The desired result is then obtained by adding the percentages found for the whole numbers and for the decimals. Thus, had the titration given 106·78 per cent. H_2SO_4, the percentage of trioxide

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[1] *Z. angew. Chem.*, 1896, **9**, 453.

[2] *Ber.*, 1901, **34**, 4114.

[3] *Z. anal. Chem.*, 1899, **38**, 167.

present in the oleum would be $26{\cdot}657 + 3{\cdot}465 = 30{\cdot}12$ per cent. The corrections for SO_2 and fixed residue must, of course, be made as described (p. 391), before making use of these tables.

Table for finding the Percentage of Free SO_3 in Oleum from the Total SO_3 as determined by Analysis. Knietsch.

SO_3		SO_3		SO_3		SO_3		SO_3		SO_3	
Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.
81·63	0·0	84·7	16·7	87·8	33·6	90·9	50·5	94·0	67·3	97·0	83·7
81·7	0·4	84·8	17·2	87·9	34·1	91·0	51·0	94·1	67·9	97·1	84·2
81·8	0·9	84·9	17·8	88·0	34·7	91·1	51·6	94·2	68·4	97·2	84·8
81·9	1·5	85·0	18·3	88·1	35·2	91·2	52·1	94·3	69·0	97·3	85·3
82·0	2·0	85·1	18·9	88·2	35·8	91·3	52·6	94·4	69·5	97·4	85·8
82·1	2·6	85·2	19·4	88·3	36·3	91·4	53·2	94·5	70·1	97·5	86·4
82·2	3·1	85·3	20·0	88·4	36·8	91·5	53·7	94·6	70·6	97·6	86·9
82·3	3·6	85·4	20·5	88·5	37·4	91·6	54·3	94·7	71·2	97·7	87·5
82·4	4·2	85·5	21·0	88·6	37·9	91·7	54·8	94·8	71·7	97·8	88·0
82·5	4·7	85·6	21·6	88·7	38·5	91·8	55·4	94·9	72·2	97·9	88·6
82·6	5·3	85·7	22·2	88·8	39·0	91·9	55·9	95·0	72·8	98·0	89·1
82·7	5·8	85·8	22·7	88·9	39·6	92·0	56·4	95·1	73·3	98·1	89·7
82·8	6·4	85·9	23·2	89·0	40·1	92·1	57·0	95·2	73·9	98·2	90·2
82·9	6·9	86·0	23·8	89·1	40·6	92·2	57·5	95·3	74·4	98·3	90·7
83·0	7·5	86·1	24·3	89·2	41·2	92·3	58·1	95·4	75·0	98·4	91·3
83·1	8·0	86·2	24·9	89·3	41·7	92·4	58·6	95·5	75·5	98·5	91·8
83·2	8·5	86·3	25·4	89·4	42·3	92·5	59·2	95·6	76·1	98·6	92·4
83·3	9·1	86·4	26·0	89·5	42·8	92·6	59·7	95·7	76·6	98·7	92·9
83·4	9·6	86·5	26·5	89·6	43·4	92·7	60·3	95·8	77·1	98·8	93·5
83·5	10·2	86·6	27·0	89·7	43·9	92·8	60·8	95·9	77·7	98·9	94·0
83·6	10·7	86·7	27·6	89·8	44·5	92·9	61·3	96·0	78·3	99·0	94·6
83·7	11·3	86·8	28·1	89·9	45·0	93·0	61·9	96·1	78·8	99·1	95·1
83·8	11·8	86·9	28·7	90·0	45·6	93·1	62·4	96·2	79·3	99·2	95·6
83·9	12·3	87·0	29·2	90·1	46·1	93·2	63·0	96·3	79·9	99·3	96·2
84·0	12·9	87·1	29·8	90·2	46·6	93·3	63·5	96·4	80·4	99·4	96·7
84·1	13·4	87·2	30·3	90·3	47·2	93·4	64·1	96·5	81·0	99·5	97·3
84·2	14·0	87·3	30·9	90·4	47·7	93·5	64·6	96·6	81·5	99·6	97·8
84·3	14·5	87·4	31·4	90·5	48·3	93·6	65·2	96·7	82·0	99·7	98·4
84·4	15·1	87·5	31·9	90·6	48·8	93·7	65·7	96·8	82·6	99·8	98·9
84·5	15·6	87·6	32·5	90·7	49·4	93·8	66·2	96·9	83·1	99·9	99·5
84·6	16·2	87·7	33·0	90·8	49·9	93·9	66·8	...	...	...	...

Setlik[1] has described a simple and rapid method for the estimation of fuming sulphuric acid, which depends on the known property of oleum to fume in the air until all anhydride present has been converted to monohydrate. The analysis is carried out as follows. At least 50 g., or preferably 100 g., to simplify the calculation, of the sample are weighed off on an ordinary balance to within 0·1 g., into a long-necked flask of from 130 to 200 c.c. capacity, and distilled water dropped in very slowly from a tap burette graduated in $\frac{1}{10}$ c.c. and provided with a fine exit-tube.

[1] *Chem. Zeit.*, 1889, 13, 1670.

Table for finding the Percentage of SO_3 in Oleum from the Total Acidity calculated as H_2SO_4. Grünhut.

Whole Numbers.			*	Hundredth Parts.									
10	11	12		0	1	2	3	4	5	6	7	8	9
0	44·428	88·857	0	0	0·044	0·089	0·133	0·178	0·222	0·267	0·311	0·355	0·400
4·443	48·871	93·300	1	0·444	0·489	0·533	0·578	0·622	0·666	0·711	0·755	0·800	0·844
8·886	53·314	97·743	2	0·889	0·933	0·977	1·022	1·066	1·111	1·155	1·200	1·244	1·288
13·329	57·757	...	3	1·333	1·377	1·422	1·466	1·511	1·555	1·599	1·644	1·688	1·733
17·771	62·200	...	4	1·777	1·822	1·866	1·910	1·955	1·999	2·044	2·088	2·133	2·177
22·214	66·643	...	5	2·221	2·266	2·310	2·355	2·399	2·444	2·488	2·532	2·577	2·621
26·657	71·085	...	6	2·666	2·710	2·755	2·799	2·843	2·888	2·932	2·977	3·021	3·066
31·100	75·528	...	7	3·110	3·154	3·199	3·243	3·288	3·332	3·377	3·421	3·465	3·510
35·543	79·971	...	8	3·554	3·599	3·643	3·688	3·732	3·776	3·821	3·865	3·909	3·954
39·986	84·414	...	9	3·999	4·043	4·087	4·132	4·176	4·221	4·265	4·310	4·354	4·398

As the reaction is very violent, means must be provided for keeping the flask well-cooled. At the start the drops of water falling into the oleum fizz violently and give rise to dense fumes; as the titration proceeds, the reaction becomes less violent and the fumes less dense. Towards the end of the titration the shaking must be continued sufficiently long, after the addition of each drop, to allow the sulphuric acid fumes to be completely absorbed; this is necessary to permit of proper observation. The reaction is finished when no further fumes form on the surface of the acid and a drop of water falling in the centre dissolves quietly.

The calculation of the analysis is very simple: 9 c.c. H_2O saturate 40 g. SO_3, or 100 c.c. H_2O correspond to 444 g. SO_3. If, for example, 100 c.c. of oleum have been taken, and 6 c.c. of water required, the sample contains 26·64 per cent. free SO_3. A table such as the following may readily be prepared to give the content in free SO_3 directly from the titration.

c.c. Water required per 100 g. Sample.	Free SO_3	c.c. Water required per 100 g. Sample.	Free SO (SO_3)
0·1	0·444	1·1	4·882
0·2	0·888	1·2	5·332
0·3	1·333	1·3	5·777
0·4	1·776	1·4	6·221
0·5	2·222	1·5	6·666
0·6	2·664	1·6	7·101
0·7	3·110	1·7	7·544
0·8	3·551	1·8	7·996
0·9	3·996	1·9	8·440
1·0	4·444	2·0	8·888

It is advisable to have an approximate knowledge of the strength of the oleum before making the analysis, since an oleum containing over

35 per cent. SO_3 does not lend itself to direct titration, owing to the violence of the reaction. In such cases the sample should be reduced to from 30 to 35 per cent. oleum by addition of sulphuric acid monohydrate. The monohydrate used for this purpose must, of course, have been carefully prepared, and should be stored in well-stoppered bottles. Setlik recommends the method for works use, and claims that with a little practice the test is quickly carried out, and is as accurate as titration with alkali, especially if the acid be contaminated with sulphurous acid, arsenious acid, sulphate of iron, or other impurity.

Rabe's method[1] is somewhat similar in principle, but sulphuric acid of known strength (say 95 per cent.) is employed for titrating in place of the water. This substitution only complicates the method and renders the results less exact.[2]

Both methods are intended for works use only, and not for the analysis of acids intended for sale.

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[1] *Chem. Zeit.*, 1901, **25**, 345.

[2] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. i., p. 246.

THE MANUFACTURE OF SALTCAKE AND OF HYDROCHLORIC ACID

By Professor G. LUNGE ; translated by JAMES T. CONROY, B.Sc., Ph.D.

A. BRINE AND SALTWORKS

BRINE is regularly tested by the hydrometer both at the spot where it is obtained (bore-holes, etc.), and in the works where it is employed (saltworks, ammonia-soda works, etc.). The temperature at which the readings are made should of course be taken into account, and the accuracy of the hydrometer ascertained. The method of checking hydrometers, together with a description of the errors usually found in these instruments, more particularly the cheaper kinds, have already been described (*cf.* p. 156 *et seq.*).

A saturated solution of sodium chloride boils at 109°·4, and contains at this temperature between 29·4 and 29·5 per cent. of the salt.

The relationship between the specific gravity of salt solutions and the percentage content of salt, at 15° C., is given in the following table:—

Specific Gravity.	Percentage NaCl.	Specific Gravity.	Percentage NaCl.	Specific Gravity.	Percentage NaCl.
1·00725	1	1·07335	10	1·14315	19
1·01450	2	1·08097	11	1·15107	20
1·02174	3	1·08859	12	1·15931	21
1·02899	4	1·09622	13	1·16755	22
1·03624	5	1·10384	14	1·17580	23
1·04366	6	1·11146	15	1·18404	24
1·05108	7	1·11938	16	1·19228	25
1·05851	8	1·12730	17	1·20098	26
1·06593	9	1·13523	18	1·20433	26·395

H. C. Hahn[1] has more recently determined the specific gravity of solutions of sodium chloride, reducing the values to water at 4°, and observing all possible precautions. Owing to the very special refinements

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[1] *J. Amer. Chem. Soc.*, 1898, **20**, 621 ; *Chem. Centr.*, 1898, II., 699.

used in the determinations, they are hardly applicable to technical conditions of work.

ANALYSIS OF BRINES AND MOTHER LIQUORS

The following determinations are made :—

1. *Specific gravity*, by means of a densimeter or a hydrometer; in the latter case the hydrometer readings are reduced to sp. gr. by means of the table given on p. 160.

2. *Total Chlorine* (*expressed as sodium chloride*). Ten c.c. of the brine are diluted to 1000 c.c.; of this 10 c.c. are titrated with silver nitrate solution (*cf.* p. 401).

3. *Sulphuric acid.* Fifty c.c. of the brine are rendered acid by the addition of a few drops of hydrochloric acid, diluted with an approximately equal volume of water and, when hot, treated gradually with a hot solution of barium chloride. The settled precipitate is repeatedly washed by decantation with hot water, acidulated with hydrochloric acid, and finally well washed on the filter (*cf.* p. 274).

4. *Oxides of Iron, Aluminium, Calcium, and Magnesium.* Two hundred and fifty c.c. of the brine are warmed with a little nitric acid, ammonia added in excess, and the whole heated for some time; the precipitate is filtered, dissolved in hydrochloric acid, reprecipitated, and ferric oxide and alumina determined in the usual manner. The calcium and magnesium are determined in the filtrate as described on p. 405. The calculation of the analytical results is made in exactly the same manner as in the analysis of salt (p. 402).

5. *Bicarbonates of ferrous Iron, Calcium, and Magnesium.* Five hundred c.c. of the brine are boiled fairly vigorously in a tall beaker or Erlenmeyer flask, fresh water added, and the boiling and evaporation repeated several times. Finally, hot water is added to the highly concentrated solution to dissolve any separated salt, the solution filtered, the insoluble residue washed with hot water, dissolved in hydrochloric acid, and precipitated with ammonia solution, free from carbonate. The precipitation is repeated if necessary. The precipitate of ferric hydroxide is filtered off, dissolved whilst still moist in dilute sulphuric acid (1 : 4), and the undiluted reduced solution titrated with permanganate solution, and the volume of permanganate necessary to produce a faint rose coloration in the solution alone deducted from the reading obtained. Calcium and magnesium are determined in the filtrate as described on page 405 *et seq.* The bicarbonates found are entered in the analysis as carbonates, and the quantity so found must be deducted from the total calcium, magnesium, and ferric oxide obtained under 4, before calculating the rest of the calcium and magnesium to sulphates or chlorides. Calcium bicarbonate is, as a rule,

present to an appreciable extent in brine (from 0·2 to 0·5 g. and more per litre); on the other hand, magnesium bicarbonate appears in much smaller quantity, and its estimation may, as is usually the case in works testing, be neglected.

6. *Water.* The percentage of water is arrived at by deducting the sum of the weights of the solid constituents present in a litre, from the weight of the litre of brine.

The results are calculated on the litre of brine or mother liquor.

B. SODIUM CHLORIDE (ROCK SALT)

Sodium chloride melts, according to Carnelly,[1] at 772°; according to v. Meyer and Riddle,[2] at 815°·4.

The commercial products may contain, in addition to moisture and water of hydration combined with calcium sulphate, etc., the following impurities: chlorides of calcium, magnesium, and potassium; sulphates of calcium, sodium, magnesium, and potassium; magnesium carbonate, organic substances (bitumen, mineral oil), gaseous hydrocarbons, and clay. According to the nature of the clay content, which seldom exceeds 0·1 per cent., the salt is coloured usually a bluish green, but sometimes yellow, brown, reddish brown, or greenish (Schwarzenberg).

Other impurities which occur less frequently and only in traces, are: potassium bromide, potassium iodide, and lithium chloride, all of which, in consequence of their relatively greater solubility, accumulate in the mother liquors. Thus Krauch found in the concentrated mother liquors of brine from Werl 3·3754 g. KBr, 0·0137 g. KI, and 8·9833 g. LiCl, per litre. Magnesium borate is found admixed with rock salt at Stassfurt. Occasionally the percentage of soluble foreign salts present is so great that the rock salt is rendered useless for food purposes.

An appreciable percentage of magnesium chloride (0·2 per cent. is sufficient) gives a sharp saline flavour to the salt and renders it hygroscopic. Distinct amounts of calcium chloride also make the salt hygroscopic.

The following methods of analysis apply to ordinary salt, and to pure sodium chloride intended for analytical purposes, respectively.[3]

1. ORDINARY SALT

Sampling. For the method of taking an average sample, *cf.* p. 13.

Qualitative analysis. The salt is, from time to time, examined

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[1] *J. Chem. Soc.*, 1879, **35**, 280. [2] *Ber.*, 1893, **26**, 2447.

[3] A description of the analysis of "Denatured Salt" is included in the German edition, vol. i., p. 409.

qualitatively for potassium, alkali bromides, and iodides, and, when it is intended for culinary purposes, also for metallic salts (lead, copper, tin) which may have been taken up from the vessels used in the purification process. These metals are detected in the usual manner. A simple method of examining for the other impurities mentioned consists in extracting a considerable quantity of the salt with water, using an insufficient quantity to effect complete solution, evaporating the filtered extract to one-third of its bulk, again filtering, and dividing the filtrate into two portions. To the first portion platinic chloride is added and the mixture thoroughly shaken; a lemon yellow precipitate indicates the presence of potassium chloride. The second portion is treated with chlorine water, drop by drop, and shaken with chloroform before each fresh addition; any iodine present is liberated first, the bromine subsequently, and each may be recognised in turn by the colour imparted to the chloroform. (*Cf.* also p. 404 for Krauch's method of testing for iodine.)

Quantitative analysis. For works' purposes a shortened method of analysis is usually adopted. The constituents generally estimated are moisture, total chlorine, expressed as sodium chloride, sulphuric acid, calculated to calcium sulphate, and matter insoluble in water. These figures are amplified periodically by the estimation of calcium, magnesium, ferric oxide, and of the percentage insoluble in hydrochloric acid whereby the percentage of sand and clay is obtained, and also, by difference, the approximate amounts of calcium and magnesium carbonates present (cf. *infra*). The quantities of magnesium chloride and of sodium sulphate, or calcium chloride, present may be arrived at by the following simple methods, which will be found sufficiently accurate for technical purposes.

1. Water.—(*a*) *Moisture.* Five g. of the salt are heated in a platinum crucible, well covered to prevent loss by decrepitation, at first very gradually and finally for some minutes at a low red heat. The loss in weight gives the total water present, that is, the moisture proper plus that chemically combined; the amount of the latter is usually very small. This method has the disadvantage that, no matter what care be taken, a small loss of salt always occurs owing to the unavoidable decrepitation. By employing as new a platinum crucible as possible, with smooth walls and a well-fitting lid, and placing the stand, Bunsen burner, etc., on a sheet of black glazed paper, the loss, which may reach 1 per cent. or over, is very much diminished; but the method lacks certainty and cannot be carried out quickly or without direct attention. In works where dozens of water estimations, including those of damp salt, which may contain up to 15 per cent. of water, have to be made, the inaccuracy of the above method is very pronounced, especially in cases where the salt contains over 7 or 8 per cent. of water, as the decrepitation is then greater.

Böckmann consequently recommends the following method, which, whilst perfectly accurate, permits of a large number of water determinations being made simultaneously and without special attention during the drying process.

A small, perfectly dry Erlenmeyer flask, about 14 to 15 cm. high, and of about 250 c.c. capacity, is weighed together with a dry funnel inserted in the neck. About 5 g. of salt are then introduced into the flask, this quantity being just sufficient to form a thin layer on the bottom, and the flask, funnel, and salt accurately weighed. The object of the funnel is to allow the dried salt to be cooled in the open instead of in a desiccator, and to prevent loss of salt by decrepitation during the expulsion of the combined water described under *b*. The flask is then placed on a previously warmed, portable sand-bath, 40 cm. by 20 cm., and large enough to carry eight flasks, the temperature of the sand being about 140° to 150°. The funnels are removed, and placed, each near its corresponding flask, on the bench. The water soon begins to come off, condensing at the start on the upper portions of the flasks; at the end of three to four hours all the water present as moisture is driven off from the salt without any crackling sound. The funnels are replaced in the flasks, which are then allowed to cool on a thick glass or marble slab, and weighed.

(*b*) *Chemically combined Water*. After the determination of the moisture the flasks are carefully heated on a wire gauze, or on a metal (aluminium) plate, over the free flame, with the funnels in position, to prevent loss by decrepitation. The water held in chemical combination by calcium sulphate, etc., is thus driven off; the evolution of this small quantity of water is accompanied by violent crackling. Since the amount of combined water present is very frequently under 0·1 per cent. and seldom more than $\frac{1}{4}$ to $\frac{1}{3}$ per cent., its determination can generally be omitted in technical analyses.

2. **Total Chlorine (expressed as Sodium chloride).**—Ten g. of the finely ground average sample are dissolved in lukewarm water, and after cooling, made up to 500 c.c. at 15° in a graduated flask. Ten c.c. of this solution, corresponding to 0·2 g. salt, are diluted with 100 c.c. of water, 10 drops of a 10 per cent. potassium chromate solution added, and the whole titrated with silver nitrate solution (p. 123). A deduction of 0·2 c.c. silver nitrate solution is made from the observed reading, since this quantity is necessary to produce the red colour with the chromate. Each 1 c.c. *N*/10 silver nitrate solution equals 0·005850 g. NaCl. If 5·850 g. of salt are dissolved to 500 c.c., and 25 c.c. of this solution taken for the titration, the percentage of sodium chloride in the salt is obtained on multiplying by 2 the number of c.c. taken.

3. **Sulphuric acid.**—Ten g. of the sample are dissolved in lukewarm water and a little hydrochloric acid added; should much earthy matter

be present the salt should be digested for some time with hydrochloric acid, to ensure complete solution of the calcium sulphate present. The cooled solution is then made up to 500 c.c. and passed through a dry, pleated filter. Two hundred and fifty c.c. of the filtrate are heated to boiling and precipitated by the addition of hot barium chloride solution in slight excess. The barium sulphate is first washed by decantation with water acidulated with hydrochloric acid, and finally on the filter (*cf.* p. 274).

4. **Matter insoluble in water and acids, Calcium and Magnesium.**—Fifty g. of the finely ground average sample are dissolved in warm water and filtered through a filter paper previously tared against one of equal weight (p. 28). The insoluble matter is carefully washed from the filter into a small glass mortar and ground with sufficient water to dissolve all the gypsum present. The water is decanted and the operation repeated a few times. The insoluble matter is again collected on the filter and dried at 100°; the weight obtained represents the matter insoluble in water (clay, sand, oxide of iron, calcium carbonate, etc.). This residue is then treated on the filter with warm dilute hydrochloric acid, the solution obtained precipitated by the addition of ammonia, the precipitated ferric hydroxide dissolved in dilute sulphuric acid (1 : 4), and the iron estimated, after reduction by zinc, by titration with permanganate solution. The direct titration of the hydrochloric acid extract, after reduction, in presence of manganese sulphate (20 c.c. of a 20 per cent. solution), yields less accurate results owing to the lack of sharpness of the end-reaction. The residue insoluble in hydrochloric acid is well washed with water, dried at 100°, and weighed to give the percentage of sand and clay. The difference between the sum of the weights of the sand, clay, and iron oxide, and the weight of the total matter insoluble in water, may usually be regarded as representing the carbonates of calcium and magnesium present.

The calcium and magnesium are determined in the filtrate from the insoluble matter in the usual manner after addition of ammonium chloride and ammonia (*cf.* p. 405).

Calculation of Results. All magnesium found is calculated to magnesium chloride and its equivalent in sodium chloride deducted from the "total" sodium chloride, to give the actual content of the latter. Should more sulphuric acid be found than corresponds to the soluble calcium, such excess is calculated to sodium sulphate. In the reverse case the excess of calcium is calculated to calcium chloride, and a corresponding deduction made in arriving at the percentage of sodium chloride.

J. and S. Wiernik[1] recommend a direct determination of the magnesium chloride present in sodium chloride and in brine, and they

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[1] *Z. angew. Chem.*, 1893, **6**, 43.

further state that wholly incorrect results may be obtained by the usual method of calculation. They extract the dried salt with absolute alcohol, which dissolves out magnesium chloride only, and, after evaporating off the alcohol, estimate either the magnesium as pyrophosphate or the chlorine by titration. Both methods should give the same result when expressed as magnesium chloride. The total calcium, magnesium, chlorine, and sulphuric acid are estimated in the original solution in the usual manner. The sulphuric acid found is first calculated on the calcium, then on the excess of magnesium that may be present above that found as magnesium chloride by extraction with alcohol; any sulphuric acid still remaining is regarded as existing as sodium sulphate. Chlorine found as magnesium chloride is deducted from the figure obtained for "total chlorine," and the difference stated in terms of sodium chloride.

All such calculations are quite illusory in the case of dilute solutions where the salts are either almost completely ionised or in part dissociated hydrolytically; in the case of solid salts and concentrated solutions such as the above, however, the greater part of the salts are actually present as such.

2. Pure Sodium Chloride for Analytical Purposes

According to Krauch, pure sodium chloride appears under the following names: Natrium chloratum chem. pur., natrium chloratum puriss., natrium chloratum puriss. exsicc., natrium chloratum puriss. fus. The natr. chlorat. chem. pur. is absolutely pure; the various varieties of natr. chlorat. "puriss." are generally sufficiently pure for analytical purposes, but not always so, a point to be borne in mind in standardising silver nitrate solution. These preparations usually contain traces of sulphates of calcium or magnesium. Kubel[1] found magnesium chloride and ammonium chloride in commercial natr. chlorat. pur.

Krauch's method of examining natr. chlorat. chem. pur. is as follows:—

Complete Solubility and freedom from Sulphate.—Three g. of salt and 20 c.c. of water should yield a clear, neutral solution, which, when diluted to 80 c.c., heated to boiling, and treated with barium chloride, should show no signs of a precipitate even after standing for several hours.

Examination for Alkaline Earths and heavy Metals.—Three g. of the salt are dissolved in 50 c.c. of water, the solution heated to boiling, and ammonium oxalate, sodium carbonate, and ammonium sulphide added. No turbidity should result.

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[1] *Arch. Pharm.*, 1888, **226**, 440.

Iodine.—Twenty c.c. of the aqueous solution (1 : 20) treated with one drop of ferric chloride solution and a little starch solution should show no blue coloration.

Potassium.—The concentrated solution of the salt should give no precipitate on addition of platinic chloride even after long standing.

C. SULPHURIC ACID

The examination of sulphuric is conducted as previously described (p. 359 *et seq.*). The acid employed in the manufacture of saltcake is either non-purified chamber acid, Glover acid, or acid concentrated in pans placed over the pyrites burners. The acid employed in the preparation of saltcake intended for use in the manufacture of the better qualities of glass should be as far as possible free from iron. The estimation of iron is described above (p. 380 *et seq.*).

D. SALTCAKE

The saltcake drawn from the furnaces is spread out in long ridges on a stone-paved floor to cool. Samples are taken morning and evening, corresponding to the output of each furnace, from various places in the several rows, and an average of the lots so taken ground in a suitable mill.

The judging of the sample by its appearance is described later under the Leblanc soda process (p. 422).

For works' purposes, estimations 1 and 2 given below are sufficient; for purposes of sale or purchase, the other tests given should be made.

1. **Free Acid.**—Twenty g. of the saltcake are dissolved in water and made up to 250 c.c.; 50 c.c. of this solution are titrated with normal sodium hydroxide solution, using litmus or methyl orange as indicator. Each 1 c.c. alkali corresponds to 1 per cent. SO_3. All acidity, whether arising from HCl, $NaHSO_4$, or from iron and aluminium salts of acid reaction, is calculated to SO_3. Should large quantities of iron and aluminium salts be present, and it be desired to avoid the influence of these in this determination, no special indicator is added to the solution, and the end-reaction is judged by the first appearance of a permanent flocculent precipitate, which occurs as soon as the free acid and the acid sulphate have been neutralised by the alkali.

2. **Sodium chloride.**—Fifty c.c. of the solution prepared under 1 are exactly neutralised by the addition of the necessary volume of normal sodium hydroxide solution, and the neutral solution titrated with $N/10$ silver nitrate solution after the addition of a little potassium

chromate solution (*cf.* p. 123). Each 1 c.c. silver nitrate solution, after deducting 0·2 c.c. from the total as allowance for the end-reaction, corresponds to 0·146 per cent. NaCl. Or a solution containing 2·9054 g. $AgNO_3$ per litre may be employed, each 1 c.c. of which corresponds to 0·001 g. NaCl, or, with the above amount of saltcake, to 0·025 per cent. NaCl. This weaker silver nitrate solution should always be used in the case of high-grade saltcake.

3. **Iron.**—Ten g. of the sulphate are dissolved in water, the iron reduced by addition of zinc and sulphuric acid and titrated with permanganate solution (p. 380). Very small amounts are estimated colorimetrically (p. 381). According to Ost,[1] sulphate manufactured in lead pans contains from 0·009 to 0·029 per cent. Fe; that manufactured in iron pans 0·062 to 0·130 per cent. Fe.

4. **Insoluble Matter** when present is estimated in the usual way.

5. **Calcium.**—Ten g. of the saltcake are dissolved in water, a little hydrochloric acid being added if necessary, and the solution treated with ammonium chloride and ammonia, the latter in slight excess. The ammoniacal solution is heated to boiling and the calcium precipitated by the addition of a boiling solution of ammonium oxalate in considerable excess. The solution is allowed to stand for twelve hours, and the precipitate then washed with boiling water several times by decantation and finally on the filter, a small quantity of ammonium oxalate being added to the wash-water. The filter paper and precipitate are dried and burnt off in a platinum crucible (this may be done whilst the precipitate is still slightly moist), after which the whole is strongly ignited for twenty minutes over a Müncke or Teclu burner. Should the precipitate be large in amount, which is not likely to be the case, it must be heated in the blowpipe flame until the weight becomes constant. The precipitate is regarded as CaO; any ferric oxide present must, of course, be deducted. The desiccator used must be protected, to prevent access of moisture and carbonic dioxide (p. 29).

Should any considerable quantity of magnesium be present—which is never likely to occur, however, in saltcake—the washed calcium oxalate precipitate must be transferred to a beaker, dissolved in a little warm hydrochloric acid, and reprecipitated by the addition of 2 to 3 c.c. of ammonium oxalate followed by ammonia in slight excess. The precipitate is allowed to settle for twelve hours and the reprecipitated calcium oxalate treated as above. The two filtrates are then combined for the magnesium determination.

Instead of converting the calcium oxalate to oxide and weighing, it has been recommended to dissolve the precipitate in dilute sulphuric acid and to titrate with permanganate solution, calculating the calcium from the oxalic acid thus found. Of course, in this case it is inadmis-

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[1] *Z. angew. Chem.*, 1896, **9**, 9.

sible to add ammonium oxalate to the water employed for washing; on the other hand, such omission may lead to a loss which is by no means negligible. Walland[1] overcomes this difficulty by standardising the permanganate solution against calcium oxalate prepared from pure calcium oxide obtained by ignition of the carbonate, and treated in exactly the same way as the precipitate obtained in the actual analysis, so that the errors are the same in the two cases.

Such a method always has disadvantages, and is only to be recommended when, as in technical work, a large number of analyses have to be made simultaneously; when this is not the case it offers no saving of time as compared with the ordinary method by ignition.

6. **Magnesium** is estimated by addition of ammonium phosphate to the filtrate from operation 5. For very exact work this addition should be made in neutral solution and as far as possible in the absence of ammonium salts, the necessary ammonia being added subsequently. The filtrate from 5 should therefore be evaporated to dryness and, after gentle ignition to drive off the ammonium salts, extracted with a small quantity of hydrochloric acid. The solution is filtered from any separated carbonaceous matter, exactly neutralised with ammonia, heated to boiling, and sodium phosphate solution added, drop by drop, to the boiling solution until no further precipitation results. The mixture is allowed to cool, ammonia solution equal to one-third of its volume added, and the whole allowed to stand for three hours, or should only a small amount of magnesium be present, for twelve hours, before filtering. The precipitate is washed with 2½ per cent. ammonia solution, dried, separated as completely as possible from the filter paper, the latter burnt separately in a spiral of platinum wire, and the ash and precipitate then ignited, first at a low heat and finally strongly. The precipitate is thus converted to pyrophosphate, $Mg_2P_2O_7$, one part of which corresponds to 0·3624 g. MgO.

In the analysis of saltcake it is usual to precipitate the magnesium by direct addition of sodium phosphate to the filtrate from 5 without removing the ammonium oxalate, and observing the other precautions given; in this case the precipitate should be allowed to stand twenty-four hours before filtering.

This method of separating calcium and magnesium is essentially in accord with the conditions given by Treadwell.[2] An alternative method, differing somewhat from the above, has been described by T. W. Richards.[3] The magnesium salts must not be present in the solution in greater concentration than corresponds to $\frac{1}{50}$ normal. Ten equivalents of ammonium chloride are added to the solution, followed by oxalic acid in sufficient quantity to combine with the whole of the calcium. It is

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[1] *Chem. Zeit.*, 1903, **27**, 922.

[2] *Analytical Chemistry*, vol. ii., p. 70.

[3] *Z. anorg. Chem.*, 1901, **28**, 88.

advantageous to reduce the dissociation of the oxalic acid by the previous addition of three or four equivalents of hydrochloric acid. A drop of methyl orange is added, the solution boiled, and very dilute ammonia added gradually at suitable intervals and with continued stirring; the addition of the ammonia solution should occupy half an hour. When the solution has been made neutral, a large excess of ammonium oxalate is added, and the whole allowed to stand for four hours. The precipitated calcium oxalate is thoroughly washed with water containing ammonium oxalate. The filtrate contains the whole of the magnesium with the exception of 0·1 to 0·2 per cent., which causes a corresponding error in the calcium, the whole of which is contained in the precipitate.

Heraeus[1] states that platinum crucibles are easily injured by the ignition of magnesium ammonium phosphate, both in the case of pure platinum and of platinum-iridium. The effect takes place, however, in a very irregular manner, and is to be attributed to the liberation of phosphorus, which occurs at 900°, arising partly from the presence of carbon or reducing gases, and also partly from the hydrogen liberated by the decomposition of ammonia at the high temperature. The action due to ammonia is stronger if free ammonium phosphate be present in the precipitate, and may very easily occur if Gooch crucibles are used in which old precipitates have been allowed to remain. The action is most marked when the heating is carried out rapidly in a covered crucible. Up to the present it has not been possible to define the conditions under which the crucibles are least attacked.

A rapid, and for many purposes sufficiently exact, method of determining calcium and magnesium consists in adding sodium carbonate to the filtrate from the silica, ferric oxide, and alumina, evaporating to dryness, igniting to remove the ammonium salts, taking up with sodium carbonate solution, extracting with hot water and weighing the calcium and magnesium carbonates remaining in the dish after drying at 200°; or by weighing as $CaO + MgO$ after ignition. The quantity of each base present may be determined indirectly from the difference in weight between the $CaCO_3 + MgCO_3$ and the $CaO + MgO$; it is, however, better for this purpose to convert both into the sulphates. Christomanos[2] has applied this method to the analysis of a large number of samples of magnesite. It must, however, be borne in mind that this, like all other indirect methods, may lead to somewhat large errors.

7. Aluminium.—A considerable quantity of ammonium chloride or of ammonium nitrate is added to the solution of the saltcake, the mixture heated nearly to boiling in a porcelain or platinum dish and ammonia added, but not in too great excess, as the removal of an excess by boiling off is not only unnecessary but harmful; the precipitate is then

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[1] *Z. angew. Chem.*, 1902, **15**, 917.

[2] *Z. anal. Chem.*, 1903, **42**, 606.

washed three times by decantation with hot water to which one drop of ammonia has been added, washed out on to the filter paper, thoroughly washed with hot water, and dried on the pump (*cf.* p. 273). Any small quantities adhering to the sides of the dish are wiped off with a piece of filter paper. The filter paper and precipitate may be ignited, whilst still moist, in a platinum crucible, and finally ignited strongly, preferably over the blowpipe. The weight of ferric oxide, as found under 3, must be deducted from the weight obtained.

The ammonia employed must be tested by barium chloride for freedom from carbonate, which, if present, would cause precipitation of the calcium; if necessary, it should be purified by distillation over lime.

8. **Sodium sulphate.**—One g. of the sample is dissolved in water, the calcium, together with the iron, precipitated as under 5, the solution filtered, and the filtrate, after the addition of a few drops of pure sulphuric acid, evaporated to dryness. The dried residue is ignited, first alone, and again after the addition of a small piece of ammonium carbonate, and weighed. From the weight obtained there must be deducted (*a*) the sulphate equivalent of the sodium chloride found under 2 (1·000 g. $NaCl = 1{\cdot}215$ g. Na_2SO_4, or 1 c.c. $N/10$ silver nitrate solution $= 0{\cdot}00177$ g. Na_2SO_4), and (*b*) the magnesium sulphate equivalent of the magnesium found under 6 (1·000 g. $MgO = 2{\cdot}9836$ g. $MgSO_4$). The residue represents the Na_2SO_4 actually present in the original 1 g. of saltcake.

Isbert and Venator[1] proceed as follows:—About 2 g. of the saltcake are dissolved in the least possible volume of hot water; ferric oxide, alumina, calcium carbonate, and magnesium carbonate precipitated by the addition of ammonia and ammonium carbonate, the precipitate dissolved in hydrochloric acid and reprecipitated, the precipitate well washed with hot water, and the total filtrate collected in a platinum dish. The filtrate—which is about 100 c.c. in volume and contains, in addition to the sulphate, the free acid and sodium chloride—is treated with ammonium sulphate or sulphuric acid, and evaporated on the water-bath to convert the chloride into sulphate. The residue is gently ignited, to volatilise all ammonium salts, and weighed. From the weight of Na_2SO_4 so obtained the weight of sulphate corresponding to the chloride present in the original sample must be deducted.

Koninck's and Grossmann's methods are described in Lunge's *Sulphuric Acid and Alkali.*[2] The latter is, according to the author himself, subject to a constant, inexplicable error of 1·3 per cent., and consequently cannot be recommended for technical work.

According to Fenton,[3] the total sodium may be estimated in the following manner. An excess of the potassium salt of dihydroxy-

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[1] *Z. angew. Chem.*, 1889, **2**, 66.

[2] Vol. ii., pp. 91 and 92.

[3] *J. Chem. Soc.*, 1898, **73**, 167.

tartaric acid is added to a concentrated neutral solution of the sodium salt to be examined, and the mixture maintained at 0° for half an hour. The precipitated sodium salt of dihydroxytartaric acid is filtered off, washed with ice-cold water, dissolved in excess of dilute sulphuric acid, and titrated with permanganate solution, which readily oxidises the dihydroxytartaric acid. Magnesium salts do not interfere with the reaction, but ammonium salts must be excluded.

E. HYDROCHLORIC ACID

The daily control of the process in the works is confined to measuring the strength of the acid flowing from the condensers, jars, etc., and to determining the completeness attained in the absorption. The strength of the acid is measured by means of the hydrometer, and in some works tests are only taken once in the day. It is, however, preferable to allow the acid, as it leaves the plant, to flow through a glass cylinder in which the hydrometer floats; in this way the strength of the acid can be seen at any moment without drawing a sample.

It is especially important to check the amount of acid which escapes condensation and so passes into the atmosphere. Should the air be damp a practised eye can, to a certain extent, judge the degree of absorption by the appearance of the escaping vapours. Whilst white fumes are continually evolved from the open pipes of the pan condensers, even when condensation is complete, these consist entirely of steam, and may be distinguished from hydrochloric acid fume by the ease with which they are dissipated in the air. Hydrochloric acid vapour, on the other hand, forms dense white fumes, which, in a moist atmosphere, spread to form a heavy cloud over a considerable area, and persist for a considerable time. Very frequently the fumes only become apparent when the gases come into contact with the outer air.

According to the Alkali Act (1906), 95 per cent. of all the hydrochloric acid produced in a works must be condensed, and no gases are permitted to escape into the atmosphere which contain more than $\frac{1}{5}$ grain HCl per cubic foot (=0·457 g. per cubic metre), and the total acidity of all the gases present must not exceed the equivalent of 4 grains SO_3 per cubic foot (=9·15 g. per cubic metre). In these regulations the volume of the gases is reduced to 60° F. (15°·5 C.) and 30 inches mercury (almost exactly 760 mm.).

Examination of the Exit Gases.—The examination of the chimney gases is carried out in a Fletcher bellows, which serves both as aspirator and absorbing vessel. They are constructed to draw $\frac{1}{10}$ of a cubic foot of gas at one aspiration, but they should in all cases be standardised by filling with air at the normal working capacity and measuring the volume aspirated by expelling it into an inverted graduated vessel filled with water, correcting the volume obtained for temperature and pressure. In examining chimney or other gases the bellows are connected with the chimney by means of a porcelain, glass, or platinum tube, of 12 mm. diameter, which extends some considerable distance into the chimney. Both bellows and tube are first washed out with distilled water, 200 to 300 c.c. of distilled water then introduced, and the necessary number of aspirations made. The contents of the bellows are well shaken after each aspiration to allow all the acids present to be dissolved by the water. When the operation is complete, a little water is forced into the connecting tube and allowed to flow back into the bellows to wash out any acid that may have condensed in the tube. The liquid in the bellows is then washed into a porcelain dish, and if necessary filtered from soot. Any sulphurous acid present is oxidised by potassium permanganate, excess of the latter removed by a trace of ferrous sulphate, the solution neutralised by pure sodium carbonate, a little potassium chromate added, and the whole titrated with $N/10$ or $N/100$ silver nitrate solution. Each 1 c.c. $N/10$ silver nitrate solution = 0·003646 g. HCl.

In the Alkali Inspector's Report for 1898 (No. 35) an addition of hydrogen peroxide, free from chlorine, to the water put into the bellows was recommended. This addition effects the immediate oxidation of any sulphurous acid present in the gases. The total acidity is determined by titration with sodium carbonate solution, and subsequently the chloride as above, by means of silver nitrate. Certain difficulties are liable to occur when working in this manner. Thus discoloration may arise owing to incomplete oxidation of organic matter by the hydrogen peroxide, and this may under certain conditions lead to the reduction of the chromate; further, it is difficult to obtain hydrogen peroxide free from chlorine. For these reasons the process has been modified, and is now carried out as follows. The total acidity is determined as before with sodium carbonate solution and methyl orange, a few drops of potassium permanganate solution being added in cases where the solution is very dark owing to the presence of sooty matter. The neutralised solution is treated with 0·5 g. of calcium or magnesium carbonate, followed by 5 to 10 drops of a 5 per cent. ferrous sulphate solution, the mixture stirred for a minute and then decanted or filtered. The chloride is then estimated in the filtrate in the usual manner. The addition of ferrous sulphate gets rid of the organic matter which is carried down with the ferrous carbonate precipitate, and so gives a neutral solution in which the hydrogen peroxide will not exert any reducing action on the chromate; also, it precipitates the arsenic and copper which are found in testing the gases from copper-works.

The potassium permanganate, added to oxidise the organic matter, must be employed with caution, since the manganese sulphate produced may reduce the chromate, with the production of a green-coloured solution; this will, however, not occur if the solutions are neutralised as described.

Should any of the difficulties above referred to be met with, it is best to oxidise with nitric acid and estimate the chloride by Volhard's method (p. 123).

A continuous test may of course be made, as in the case of the exit gases of the sulphuric acid process (p. 335), by employing a large aspirator and selecting a suitable type of absorption apparatus (*cf.* p. 302); the flasks described in the Alkali Inspector's Annual Report for 1898 are specially suitable for this purpose.

EXAMINATION OF THE GASES IN THE HARGREAVES' PROCESS

In this process[1] the burner gases from pyrites or blende are drawn, together with steam, through hot salt, packed in iron cylinders, whereby the sodium chloride is converted into sodium sulphate, the sulphur dioxide being gradually absorbed and hydrochloric acid liberated. The progress of the reaction is followed by withdrawing and testing samples of the gases passing through the connecting pipes between adjacent cylinders. The tests are made in the following manner:—

(*a*) *Total acidity*, best estimated by Lunge's method (p. 299).

(*b*) *Sulphur dioxide*, by Reich's method (p. 300).

(*c*) *Hydrochloric acid*. The test is made in the sample taken for test *a* by titration with silver nitrate, either by Mohr's method (p. 123), or by Volhard's method (p. 123).

The content of sulphur trioxide is obtained by deducting $b+c$ from *a*.

For continuous work test, *a* or *b* may be omitted; either of these in combination with test *c* is sufficient.

PROPERTIES OF HYDROCHLORIC ACID

The strength of the acid is usually determined by the hydrometer. The use of the Twaddell scale possesses the advantage that for acids of ordinary strengths the number of the degrees Tw. and the percentage of acid in the acid are represented by practically the same figure. The following table, drawn up by Lunge and Marchlewski,[2] gives for the various specific gravities of pure hydrochloric acid the corresponding degrees on the Twaddell scale, the percentage content in HCl, the

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 238.

[2] *Z. angew. Chem.*, 1891, 4, 135.

percentage content in acid of 28°·5 Tw. and of 30°·4 Tw., and the weight of HCl per litre of the acid expressed in grams and per cubic foot expressed in pounds.

Specific Gravity of Hydrochloric Acid Solutions at 15° C., compared with Water at 4°, and reduced to vacuum.

(Lunge and Marchlewski.)

Degrees Twaddell.	Specific Gravity at $\frac{15°}{4°}$ (*in vacuo*).	100 parts by weight correspond to parts by weight of			1 litre contains grms. HCl.	1 cubic foot contains lbs. HCl.
		HCl.	Acid of Sp. Gr. 1·1425 = 28°·5 Tw.	Acid of Sp. Gr. 1·152 = 30°·4 Tw.		
0	1·000	0·16	0·57	0·53	1·6	0·10
1	1·005	1·15	4·08	3·84	12	0·75
2	1·010	2·14	7·60	7·14	22	1·37
3	1·015	3·12	11·80	10·41	32	1·99
4	1·020	4·13	14·67	13·79	42	2·62
5	1·025	5·15	18·30	17·19	53	3·30
6	1·030	6·15	21·85	20·53	64	3·99
7	1·035	7·15	25·40	23·87	74	4·61
8	1·040	8·16	28·99	27·24	85	5·30
9	1·045	9·16	32·55	30·58	96	5·98
10	1·050	10·17	36·14	33·95	107	6·67
11	1·055	11·18	39·73	37·33	118	7·35
12	1·060	12·19	43·32	40·70	129	8·04
13	1·065	13·19	46·87	44·04	141	8·79
14	1·070	14·17	50·35	47·31	152	9·48
15	1·075	15·16	53·87	50·62	163	10·16
16	1·080	16·15	57·39	53·92	174	10·85
17	1·085	17·13	60·87	57·19	186	11·59
18	1·090	18·11	64·35	60·47	197	12·28
19	1·095	19·06	67·73	63·64	209	13·03
20	1·100	20·01	71·11	66·81	220	13·71
21	1·105	20·97	74·52	70·01	232	14·46
22	1·110	21·92	77·89	73·19	243	15·15
23	1·115	22·86	81·23	76·32	255	15·90
24	1·120	23·82	84·64	79·53	267	16·65
25	1·125	24·78	88·06	82·74	278	17·33
26	1·130	25·75	91·50	85·97	291	18·14
27	1·135	26·70	94·88	89·15	303	18·89
28	1·140	27·66	98·29	92·35	315	19·64
29	1·145	28·61	101·67	95·52	328	20·45
30	1·150	29·57	105·08	98·73	340	21·20
31	1·155	30·55	108·58	102·00	353	22·01
32	1·160	31·52	112·01	105·24	366	22·82
33	1·165	32·49	115·46	108·48	379	23·63
34	1·170	33·46	118·91	111·71	392	24·44
35	1·175	34·42	122·32	114·92	404	25·19
36	1·180	35·39	125·76	118·16	418	26·06
37	1·185	36·31	129·03	121·23	430	26·81
38	1·190	37·23	132·30	124·30	443	27·62
39	1·195	38·16	135·61	127·41	456	28·43
40	1·200	39·11	138·98	130·58	469	29·24

The correct specific gravity at 15° C. may be calculated from readings made between 13° and 17° (and also for temperatures slightly below or above this range) by the aid of the accompanying short table. If the observed reading is made below 15° the values given in the table must be deducted for each 1° below the 15°; for observations made above 15° the corresponding values must be added.

Spec. Grav.	1·000—1·040:	± 0·0002
„	1·041—1·085:	0·0003
„	1·086—1·120:	0·0004
„	1·121—1·155:	0·0005
„	1·156—1·200:	0·0006

Kremers[1] has published a table giving the variations in the specific gravity of hydrochloric acid over a temperature range from 0° to 100° (normal temperature 19°·5); the most recent table is that of Fuchs.[2]

DETECTION OF IMPURITIES[3]

1. *Residue.** Ten g. should leave not more than a very minute and scarcely weighable residue on evaporation.

According to Krauch, the preparation of absolutely chemically pure hydrochloric acid is attended by considerable difficulties; he invariably found, on evaporating 50 g. of the acid in a porcelain dish, a residue of about 1 mg., probably consisting of calcium oxide derived from the porcelain vessel or from the sulphuric acid.

2. *Sulphuric acid.** (*a*) Five g. are diluted with 50 c.c. of water, and barium chloride added; no sign of a precipitate should appear after twelve hours' standing.

(*b*) Five hundred g. are slowly evaporated on the water-bath till only about 1 c.c. remains and the sulphuric acid estimated in this residue, an ash-free filter paper being employed. The weight of barium sulphate found should not exceed 12 mg., corresponding to 1 mg. H_2SO_4 per 100 g. hydrochloric acid.

Krauch states that scarcely a single sample of the various makes to be found on the market appears to be absolutely free from sulphuric acid when tested as under *b*; many of the samples examined gave the sulphuric acid reaction with test *a*, that is, without evaporating off the hydrochloric acid, showing, therefore, a greater degree of impurity than should be accepted.

In commercial work the evaporation of the acid may be omitted and much time saved by nearly neutralising the acid with pure sodium carbonate (not with ammonia) before precipitating by addition of barium chloride. Each one part by weight $BaSO_4 = 0·3429$ parts SO_3.

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[1] *Pogg. Ann.*, 1859, **108**, 115.

[2] *Z. angew. Chem.*, 1898, **11**, 753.

[3] The tests marked with an asterisk are due to Krauch and apply only to acid. hydrochloric. purum. conc.

A rapid method for the approximate estimation of the sulphuric acid present, well suited to works purposes, has been proposed by Lunge. The method is based on the degree of turbidity produced by addition of barium chloride, and is best carried out in the following modified form proposed by Rürup.[1] Glass tubes having a lower part 6 mm. diameter, sealed below, and an upper part 15 mm. diameter, closed with a rubber stopper, are used for the estimation; the cylindrical, narrower portion is 250 mm. in length, and is graduated in the following manner. Acids containing varying proportions of sulphuric acid, from 0·4, 0·6, etc., to 3·0 per cent. SO_3, are prepared, 10 c.c. of each heated to boiling, transferred to the tube, nearly neutralised with strong ammonia, precipitated by addition of hot barium chloride solution, and allowed to settle. A mark is then made on the tube corresponding to the level of the settled precipitate and the corresponding percentage of acid etched at the side. To carry out a test, 10 c.c. of the acid are nearly neutralised with ammonia, heated to boiling, transferred to the tube, 5 c.c. of a saturated solution of barium chloride added, the rubber stopper inserted, and the tube well shaken. Five minutes are allowed for settling before reading off the volume of the precipitate. The method is said to be accurate to within 0·05 per cent.

3. *Arsenic.* The detection and estimation of arsenic in hydrochloric acid is of importance not only in chemico-legal investigations but also in numerous analytical and technical applications. The methods of estimating arsenic in sulphuric acid apply also to hydrochloric acid (*cf.* p. 362 *et seq.*).

(*a*) According to Krauch, hydrochloric acid which will satisfy the following test may be looked upon as sufficiently pure for most analytical work. Ten g. of the acid are diluted with 10 c.c. of water and the mixture carefully covered in a test tube with a layer of 5 c.c. of freshly prepared sulphuretted hydrogen water; no coloration or yellow ring should appear at the junction of the two solutions even after the lapse of an hour. The test should be applied to both cold and hot solutions so as to detect arsenic acid; 0·000005 g. As in 1 g. acid can be detected, that is, $\frac{1}{20}$ mg. As in the quantity taken for the test.

(*b*) According to the German Pharmacopœia, III., 1 c.c. of hydrochloric acid is treated with 3 c.c. of stannous chloride solution, prepared by rubbing to a cream five parts of crystallised stannous chloride and one part of hydrochloric acid, saturating with dry hydrochloric acid gas, and filtering. No coloration should appear after the mixed solutions have stood for one hour.

(*c*) Hager's Kramato-method[2] is extremely sensitive, and quickly and simply carried out. One c.c. of the hydrochloric acid is diluted with 2 c.c. of water and a little ammonium oxalate added. A drop of the

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[1] *Chem. Zeit.*, 1894, **18**, 225.

[2] *Pharm. Centr.*, 1884, 265.

solution is then evaporated on a strip of brass (previously rubbed clean with sand and water and dried), the heating being so regulated that no ammonium salts are volatilised. If arsenic be present, a stain is produced varying from grey through red to black, according to the quantity of arsenic in the acid.

(*d*) A delicate method for the detection of arsenic has been described by Schlickum.[1] If a minute crystal (0·01 to 0·02 g.) of sodium sulphite is added to a solution of 0·3 to 0·4 g. stannous chloride in 3 to 4 g. of hydrochloric acid, both sulphur dioxide and sulphuretted hydrogen are evolved, the latter being due to the reducing action of the stannous chloride on the sulphurous acid. If hydrochloric acid containing arsenic be carefully introduced so as to form a layer on the top of the solution, a yellow ring of arsenious sulphide immediately forms at the zone of contact. The reaction is given by $\frac{1}{20}$ mg. of arsenious acid. The ring gradually extends in an upward direction, and in the presence of $\frac{1}{2}$ mg. of arsenious acid the whole of the acid layer assumes a yellow colour in the course of a few minutes. The reaction proceeds more slowly when the arsenic is present in the arsenic condition. The success of this test depends on the use of a minimum quantity of sodium sulphite and of strong hydrochloric acid, so as to prevent the separation of antimony sulphide.

The two following tests are especially adapted for confirming the complete absence of arsenic in hydrochloric acid, more particularly in chemico-legal inquiries.

(*e*) Otto's method.[2] Several litres of the acid are treated with a few crystals of potassium chlorate, and sufficient water added to reduce the specific gravity to a maximum of 1·104. The solution is evaporated on the water-bath in a porcelain dish, the residue taken up with water and examined by the Marsh-Berzelius test.

(*f*) Gutzeit's test (p. 374) is extremely delicate and allows the detection of $\frac{1}{1000}$ mg. As_2O_3, but it involves the careful observation of the conditions referred to in connection with sulphuric acid, since sulphuretted hydrogen, hydrogen phosphide, and antimoniuretted hydrogen affect both silver nitrate and mercuric chloride papers in a similar manner to arseniuretted hydrogen.

Quantitative determination of Arsenic. The arsenic present in ordinary, non-purified, commercial hydrochloric acid, may be determined quantitatively either by reducing 20 g. of the acid with sulphurous acid, driving off the excess of the latter, neutralising with sodium carbonate, and titrating with iodine or by precipitating with sulphuretted hydrogen, and weighing the sulphide obtained after extraction with carbon bisulphide. Neither method is free from objection, and in the latter case it is difficult to be certain that the arsenic is actually present

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[1] *Analyst*, 1886, **11**, 19.

[2] *Ausmittelung der Gifte*, 1884, p. 146.

as pure As_2S_3. Kretzschmar[1] therefore recommends the following method:—

The highly diluted acid is nearly neutralised by addition of sodium carbonate, ammonia and yellow ammonium sulphide then added, followed by chemically pure hydrochloric acid in excess and a strong current of sulphuretted hydrogen passed for two hours through the solution, which is kept hot on the water-bath. By this treatment the precipitation, which otherwise requires from fifteen to twenty-four hours, is complete in the time stated. The precipitate of arsenious sulphide is washed, dissolved in potassium hydroxide, aided by chlorine, or preferably by bromine, and the arsenic finally precipitated in slightly acid solution by the addition of ammonia and magnesia mixture and weighed as magnesium pyroarsenate. This method may also lead to erroneous results; should the ignition be too strong, arsenic may be distilled off, whilst if too gentle, the conversion to the pyroarsenate is likely to be incomplete.[2]

The following abnormally high percentages of arsenic found by Buchner in certain non-purified acids, viz., 2·4, 3·1, 10·4, 0·7, 4·7, 5·7, 9·7 g. As per 100 kilos crude acid have been stated[3] to be quite misleading, at all events for well-regulated works.

4. *Iron.** Five g. diluted to 25 c.c. should yield no coloration on the addition of a few drops of potassium thiocyanate solution.

For detecting traces of iron in strong acids, Venable[4] recommends making use of the blue solution obtained on treating cobaltous nitrate with strong hydrochloric acid. Traces of ferrous salts change the blue colour of such a solution to green; ferric salts are without effect.

For quantitative work the iron is reduced with zinc, the solution diluted with a large volume of distilled water, a 20 per cent. solution of manganese sulphate, free from iron, added, and the whole titrated with $N/20$ potassium permanganate solution (1·582 g. per litre), of which 1 c.c. = 0·002795 g. Fe. A blank experiment on an equal volume of the distilled water, as used above, is made at the same time and the volume of permanganate solution necessary to produce a faint permanent rose tint deducted. Traces of iron are determined colorimetrically as described above (p. 381).

5. *Sulphurous acid.* According to Krauch, the addition of a few c.c. of the diluted acid should not destroy the faint blue colour of water to which a little iodine and starch solution have been added. In the absence of chlorine and ferric chloride, sulphurous acid may also be detected by means of sulphuretted hydrogen (white cloudiness due to separated sulphur) or by stannous chloride (brown precipitate of stannous sulphide). For quantitative work, titration with permanganate or iodine solution

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[1] *Chem. Zeit.*, 1891, **15**, 269.

[2] *Cf.* Blattner and Brasseur, *Chem. Zeit.*, 1904, **28**, 211.

[3] *Chem. Zeit.*, 1891, **15**, 43.

[4] *Z. anal. Chem.*, 1889, **28**, 699.

is adopted. It is, however, safer to estimate the total sulphuric acid present after oxidation by the above reagents, or by hydrogen peroxide, and to deduct from this the sulphuric acid originally present as found under 2.

6. *Simultaneous examination for Sulphurous and Arsenious acids.* If on adding iodine solution to the acid the iodine is decolorised, at least one of these impurities is present.

Should this be the case, Hilger[1] recommends the addition of more iodine solution till an excess is present; the acid is then transferred to a test tube and a few pieces of zinc added. The test tube is loosely stoppered by a cork carrying a piece of silver nitrate paper; arsenic, if present, produces a darkening of the paper, owing to the arseniuretted hydrogen evolved. Should no darkening occur, the original acid is tested for sulphurous acid by first precipitating the sulphuric acid by means of barium chloride and adding iodine solution to the filtrate till a coloration is produced; should sulphurous acid be present in the original hydrochloric acid, a further precipitation of barium sulphate will take place.

7. *Chlorine.* No blue coloration should result when 1 c.c. of the acid, diluted with water, is added to 5 c.c. of very dilute freshly prepared starch solution to which a few drops of potassium iodide solution and a few drops of dilute sulphuric acid have been added. By carrying out the test in this manner any blue coloration due to the presence of iodate in the potassium iodide would appear before the addition of the hydrochloric acid to be tested. An alternative method of testing is to shake the acid in a closed flask with a perfectly clean, bright piece of thin copper foil, first displacing the air in the flask by means of carbon dioxide; should chlorine be present, part of the copper goes into solution and may be detected by potassium ferrocyanide, etc. For ordinary purposes it is sufficient to hold a piece of iodised starch paper in the vapours given off from the warmed acid; an immediate blue coloration shows the presence of free chlorine.

8. *Selenium* is detected by the Reinsch test and gives a similar stain on copper to that produced by arsenic; on heating the copper foil in a dry test tube a sublimate is obtained which dissolves in sulphuric acid with the formation of a brownish-green coloration.[2]

According to Reidemeister,[3] reddish-brown deposits of selenium are sometimes found in roaster acid but never in pan acid.

9. *Estimation of Hydrochloric acid.* Ten c.c. of the acid, the specific gravity of which has been previously determined, are measured from an accurate pipette, diluted to 200 c.c. with water, and 10 c.c. of this solution taken for the test; or about 1 g. of the acid is accurately weighed off in

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[1] *Jahresber. f. chem. Tech.*, 1875, p. 445.

[2] Drinkwater, *ibid.*, 1884, p. 348.

[3] Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 98.

the bulb-tap pipette (Fig. 134, p. 390), allowed to flow into water, and the whole of the solution so obtained taken for titration. The diluted solution is treated with sodium carbonate, free from chloride, until the reaction is neutral or very faintly alkaline. This may be done rapidly and without appreciable loss of acid by spotting, if sodium carbonate solution corresponding to the acid content, as determined from the specific gravity by the aid of the table given above (p. 412), be added from a burette. A little neutral potassium chromate solution is then added and the solution titrated with $N/10$ silver nitrate solution until a distinct faint rose coloration, which remains permanent on stirring, is produced (*cf.* p. 123). From the volume required, the usual deduction of the 0·2 c.c. necessary to produce the coloration must be made. The percentage of HCl in the acid is obtained by multiplying the number of the remaining c.c. by 72·92 and dividing by the specific gravity of the acid.

The titration may also be carried out by Volhard's method (p. 123).

Should metallic chlorides be present, the above method will obviously lead to incorrect results; appreciable quantities of such chlorides occur, however, but seldom. In such cases the total acidity is determined as described for sulphuric acid (p. 413), the sulphuric acid estimated as in 2, and deducted from the total acidity. This method may be employed, of course, even in the absence of metallic chlorides.

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THE MANUFACTURE OF SODIUM CARBONATE

By Professor G. LUNGE; translated by JAMES T. CONROY, B.Sc., Ph.D.

I. THE LEBLANC SODA PROCESS

RAW MATERIALS

1. SALTCAKE

THE analytical examination of saltcake has already been described (p. 404 *et seq.*). In the case of saltcake intended for alkali manufacture, additional important conclusions are to be drawn from the outward appearance and behaviour of the sulphate. According to Lunge,[1] saltcake intended for the revolver process must satisfy the following requirements. It should be very porous and in the state of fine powder, or at least "spongy"; any lumps present must be quite easily crushed with a spade, and then fall to fine powder. Hard lumps nearly always contain a core of raw common salt, which is at once recognised by its colour and texture; on crushing, its coarsely crystalline form and grey colour present a strong contrast to the fine-grained yellowish or white sulphate. Since saltcake containing salt fluxes more easily than in the pure state, pieces which are entirely fluxed, even if inwardly white, are also open to suspicion. Hard, lumpy, or fluxed saltcake, even if containing 97 per cent. of sodium sulphate, will not yield a good black ash. Sufficiently pure saltcake may be deteriorated by calcining so far that the ferric sulphate, which is always present, has been converted into red ferric oxide; such saltcake (termed "foxy") never makes good soda. Good saltcake accordingly ought to show a little, but not above 1·5 or at most 2 per cent. of free acid (as SO_3); in this case it will not, as a rule, contain more than 0·5 or at most 1 per cent. of sodium chloride. Quite fresh saltcake, just as it comes from the roaster, does not yield such good ash as that which has been lying for some time; even outwardly the difference is noticeable. Fresh saltcake always shows more or less lumps and other irregularities in texture, whilst that which has been lying for some

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[1] *Sulphuric Acid and Alkali*, vol. ii., p. 481.

time in a large heap, looks quite regular and of even grain. In all probability, in such large heaps, which retain their heat for a long time, a further reaction takes place between the undecomposed sodium chloride and the excess of acid, which improves the quality of the saltcake.

2. Calcium Carbonate

This is employed in the form of limestone, chalk, or dried lime-mud, obtained either from the Chance process (see under "Soda Residues") or from the causticising pans where the lime process is used.

So far as the revolver process is concerned, the harmful constituents likely to occur in limestone are, magnesia (dolomitic limestones are quite unsuitable), clay, sand, and iron. The last three impurities combine with the soda to form double silicates insoluble in water, and thus lead to loss of alkali. Many limestones are coloured blue and even black, owing to the presence of organic matter of a bituminous character; this impurity is, however, perfectly harmless.

The analysis is generally confined to the determination of moisture, matter insoluble in hydrochloric acid, calcium and, where necessary, magnesium. Full details are given under the manufacture of "Bleaching powder" (p. 481).

3. Mixing Slack

As a rule, coal is employed for the black ash mixture; occasionally, however, lignite, wood, charcoal, coke, etc., are used. In taking the samples for analysis, the rules given on pp. 9 and 241 must be rigorously observed. The following determinations are necessary.

1. **Moisture.**—To prevent loss of moisture during grinding, the sample is only broken down to the size of beans, and as rapidly as possible. One hundred to 200 g. are then heated for two hours at a temperature not exceeding 110°, the quantity of air entering the drying oven being kept as low as possible. If this be neglected, too great a liberation of the volatile "bituminous" constituents may occur, and finally an increase in weight due to oxidation may arise. It is advisable to employ an air-bath, the upper opening of which is nearly closed, or else a toluene vapour bath. It is still more satisfactory to heat in a current of dry carbon dioxide.

2. **Coke**, that is the non-volatile portion of the coal or fixed carbon. One g. of the finely ground coal is quickly heated in a platinum crucible, covered with a tightly fitting lid; the crucible should be at least 30 mm. deep. An ordinary Bunsen burner giving a flame at least 18 cm. high is employed, and the heating is continued so long as any appreciable quantity of combustible gas continues to escape between the crucible and the lid; this should only take a few

minutes. The crucible is then allowed to cool, and weighed. The platinum crucible should be supported in a thin wire triangle, and its bottom should not be more than 3 cm. above the top of the burner. With too small a flame, or too thick a triangle, the yield of coke comes out too high. The results are calculated on the ash-free coal or coke, to facilitate comparisons. A good fuel should yield 60 to 70 per cent. of coke.

3. **Ash.**—The estimation of the ash is very simple in the case of lignite or turf. Coke requires a very high temperature for incineration. For the determination of ash in caking coals the sample must be very finely ground and the heating effected very gradually, so that the volatile constituents may escape without the powder caking to form a coke.

Should only an occasional determination of the ash be necessary, 1 to 3 g. of the finely powdered fuel are heated in a platinum crucible supported in a hole cut in an obliquely supported piece of asbestos card (Fig. 136). By this device the air serving for oxidation is kept apart from the flame gases and the incineration is correspondingly accelerated. Working in this way, the operation is completed in two hours, whereas otherwise it might still be incomplete after eight or ten hours. The use of the blowpipe is not to be recommended, since it is liable to lead to a loss of ash mechanically.

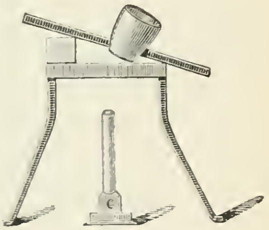

Fig. 136.

Where frequent tests have to be made it is preferable to carry out the incineration in a muffle, employing a platinum or porcelain dish; or combustion may be still more rapidly effected if the fuel, contained in a platinum boat, be heated in a porcelain tube in a current of oxygen. In the latter case small pieces of the coal or coke are taken, since with a fine powder the oxygen does not come sufficiently into contact with the lower portions.

In case a new supply of coal is to be examined, a determination of the quantity of the ash only will not be sufficient; the percentages of silica, alumina, and ferric oxide present should also be estimated according to the methods used for the analysis of silicates (*cf.* p. 580).

4. **Sulphur.**—*Eschka's method.* From 0·5 to 1 g. of the finely powdered coal is well mixed in a platinum crucible, by the aid of a glass rod, with one and a half times its weight of an intimate admixture of two parts of well-burnt magnesia and one part of anhydrous sodium carbonate, and the uncovered crucible heated in an oblique position, so that only the lower half is raised to redness. This is best done as shown in Fig. 136. The combustion is hastened by frequently stirring the mixture with a platinum wire. The colour, which is originally grey, changes during

ignition to yellow, red, or brown; the time required for the ignition seldom exceeds an hour. Hot water is then poured on the ignited mixture and bromine water added until the solution assumes a pale yellow colour, after which it is boiled, filtered, and the insoluble residue thoroughly washed with hot water. The aqueous extract is acidified with hydrochloric acid, boiled until the excess of bromine has been expelled and the solution has become colourless, and the sulphate precipitated by addition of barium chloride as described above (p. 274). Allowance must, of course, be made for any sulphate present in the magnesia and sodium carbonate mixture. Should the coal gas be rich in sulphur, it is advisable to work with a spirit lamp; Lunge, however, finds that the use of the asbestos card (Fig. 136) suffices to keep the products of combustion away from the contents of the crucible.

Hundeshagen's method differs from Eschka's in the use of potassium carbonate instead of sodium carbonate. Other published methods are either too troublesome or else too uncertain.[1] Norvicki[2] employs a Rose's crucible in carrying out the Eschka method, and so renders it possible to conduct a current of oxygen through the mixture during the operation. The application of sodium peroxide for the determination has already been described (p. 246).

5. **Nitrogen** is estimated by igniting the fuel with soda-lime, and absorbing the products formed in standard sulphuric acid as in the ordinary method of organic analysis; Kjeldahl's method (p. 247) is preferable. This estimation is much more important in the case of mixing slack than in that of furnace fuels.

CONTROL OF WORKING CONDITIONS

1. Black Ash

The outward appearance of the "ball" is a more important guide than the chemical analysis, more especially as the latter is vitiated by the impossibility of drawing a truly average sample; nevertheless analysis should of course not be omitted.

A properly made ball[3] is easily detached from the bogie. In the places exposed to the air whilst at a red heat, especially at the surface projecting from the bogie, it is of a liver-brown colour, at the other portions of the surface a blackish brown. On breaking, a good ball presents a slate-grey colour and a honeycombed, almost pumice-like structure; it should be as homogeneous as possible, with only a few particles of coal here and there. There should be no black streaks (from coal) or white

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[1] For a comparison and examination of these methods, *cf.* Heath, *J. Amer. Chem. Soc.*, 1898, **20**, 630.

[2] *Stahl u. Eisen*, 1903, **23**, 1141.

[3] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 552.

streaks (from chalk); these indicate bad working. The presence of many dispersed particles of coal or of chalk point to an excess of this constituent in the mixture. A pink or purple shade of colour is less satisfactory. The inside of a ball ought to be all of one shade, except close to the edge, where it is always a little darker.

Dark coloured balls result when the furnacing is insufficient or when the mixing has been bad. Red (burnt) balls contain much sodium sulphide, to the presence of which the colour is due.

The black ash is tested daily for its percentage of free and total lime, and for sulphide, sulphate, and carbonate of sodium; the determination of the free lime is important, since it aids the lixiviation by reason of the disruptive action brought about by hydration, and unless a certain quantity be present in the ball the lixiviation process proceeds very slowly and may be very incomplete.

Sulphide, Sulphate, and Carbonate of Sodium. In addition to the above the sodium hydroxide and chloride present are also estimated more or less frequently. The sodium found as Na_2CO_3, Na_2S, and NaOH is calculated to Na_2SO_4, and the value obtained added to that of the Na_2SO_4 present as such, giving the total sodium expressed as Na_2SO_4. By comparing this value with the figure found for "total lime," it is possible to ascertain from the analysis whether the correct proportion of saltcake and lime has been used in the mixing.

The estimation of the various constituents is carried out as follows.[1] Fifty g. of the average sample are rapidly, but thoroughly, ground in a mortar (in works it is often possible to employ some mechanical contrivance for this purpose), and introduced into a 500 c.c. flask. Lukewarm, distilled water, freed from carbonic acid by previous boiling, is then poured on the mass, which is thoroughly shaken at once, and subsequently at intervals during two hours. It is important that the mixture should be thoroughly shaken at the start, otherwise the mass cakes to a solid block on the bottom of the flask and cannot then be broken up.

1. Free Lime.—At the end of the two hours the flask is filled up to the 500 c.c. mark and two portions, each of 75 c.c., of the thoroughly mixed contents are taken for the estimation of free and total lime. For this purpose it is advisable to use a pipette, the outlet of which terminates abruptly, as shown in Fig. 137, instead of an ordinary pipette, the long narrow outlet tube of which is very apt to get blocked by the solid matter present.

FIG. 137.

The frothy material on the outside of the pipette is washed off by means of a wash-bottle, the contents emptied into a beaker and the

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 557; *Z. angew. Chem.*, 1890, 3, 570.

pipette washed out with water. An excess of barium chloride solution and a drop of phenolphthalein solution are added, and the mixture titrated with $N/5$ hydrochloric acid until the red coloration just vanishes (*cf.* p. 72). Each 1 c.c. of the acid = 0·00561 g. CaO. Provided the shaking is efficient, concordant results are obtained.

2. **Total Lime.**—This determination is carried out by first converting the lime into calcium chloride and then into calcium carbonate, in neutral solution, by addition of an excess of $N/5$ sodium carbonate solution, the excess of this reagent being titrated back by $N/5$ acid. Five c.c. of the thoroughly shaken solution, as used under 1, are treated in a small Erlenmeyer flask with a few c.c. of strong hydrochloric acid and then heated to boiling until all gas has been expelled. A drop of methyl orange is added to the cooled solution, which is then exactly neutralised with sodium carbonate solution; 30 to 40 c.c. of $N/5$ sodium carbonate are next added and the solution again heated to boiling. By this treatment the whole of the calcium is precipitated as calcium carbonate, together with a certain quantity of oxide of iron, alumina, and magnesia. The quantity of the three latter compounds is, however, small and for the present purpose may be neglected. The mixture is transferred to a 200 c.c. flask, the flask filled to the mark with water, and the excess of sodium carbonate determined by titrating 100 c.c. of the filtered solution with $N/5$ hydrochloric acid, using methyl orange as indicator.

If the number of c.c. of acid required, = n and 30 c.c. of sodium carbonate solution, have been taken, the total calcium, expressed as CaO, is = $(30-2n) \times 0{\cdot}00561$, or, expressed as $CaCO_3$, = $(30-2n) \times 0{\cdot}01001$.

The results obtained by these two tests are not to be regarded as absolute, owing to the impossibility of obtaining a really average sample; they serve, however, as a guide, provided that they are made in the thoroughly mixed turbid solution. The same reservation holds for all the results obtained for black ash, and on this account it is important to take the physical appearance of the ball into consideration (*cf.* p. 422).

After the portions for the above tests have been taken, the 500 c.c. flask is well stoppered and allowed to stand until the solution has become perfectly clear, after which portions are withdrawn for the following determinations.

3. **Total available Alkali.**—Ten c.c., = 1 g. of black ash, are titrated cold with hydrochloric and methyl orange (p. 61). This gives the total alkalinity, and is a measure of the Na_2CO_3, NaOH, and Na_2S. The quantity of Na_2CO_3 present is found by deducting the values found under 4 and 5 and is equal to 0·05305 g. for each 1 c.c. of normal acid. Any error due to small amounts of alumina and silica may be neglected.

4. **Caustic Soda** is estimated by adding an excess of barium chloride

solution (10 c.c. of a 10 per cent. solution of $BaCl_2.2H_2O$ will more than suffice) to 20 c.c. of the liquor contained in a 100 c.c. flask, filling to the mark with boiling water, shaking and corking; the precipitate settles well, the solution becoming clear after a few minutes' standing. Fifty c.c. of the clear solution are pipetted off and when cold titrated with hydrochloric acid and methyl orange. The solution should not be filtered, because filter paper absorbs appreciable quantities of barium salts. A simpler and more exact method is to titrate the solution (10 c.c.) in presence of the precipitate, employing litmus or, still better, phenolphthalein as indicator, the colour change taking place when all alkali hydroxide is neutralised (*cf.* p. 72). Each 1 c.c. of acid corresponds to 0·04003 g. NaOH in 1 g., the weight of black ash taken. In this method any sodium sulphide present is estimated as hydroxide; silica is present in such extremely minute quantity that it does not interfere with the determination, though it may do so in the case of the finished caustic soda (*cf.* p. 466).

5. **Sodium sulphide.**—Ten c.c. of the solution are diluted to about 200 c.c. with boiled air-free water, acidified with acetic acid and titrated quickly with iodine solution, employing starch solution as indicator. If $N/10$ iodine solution be used (12·697 g. I per litre), each 1 c.c. = 0·003908 g. Na_2S; if the solution be made up to contain 3·249 g. I per litre, then each 1 c.c. = 0·001 g. Na_2S. When employing the $N/10$ solution the number of c.c. required divided by 10 gives the acid equivalent to be deducted from test 4. The more exact process, due to Lestelle, described under the analysis of the finished soda ash, is unnecessary in testing black ash. A detailed investigation has been made by Marchlewski[1] on the estimation of sulphide-sulphur.

No account need be taken of other sulphur compounds, with the exception of sulphate; their separation is dealt with under Soda Mother Liquors (p. 429).

6. **Sodium chloride.**—Ten c.c. of the solution are neutralised as exactly as possible with nitric acid, most conveniently by adding the same number of c.c. of normal nitric acid (63·02 g. HNO_3 per litre) as were required of hydrochloric acid in test 3. The solution is then boiled until all sulphuretted hydrogen has been driven off, filtered from separated sulphur and, after the addition of a little neutral potassium chromate solution, titrated with silver nitrate solution. Or nitric acid of any convenient strength may be added in excess and the solution rendered slightly alkaline by addition of sodium carbonate or bicarbonate after all the sulphuretted hydrogen has been expelled. Volhard's method, using ammonium thiocyanate as indicator (p. 123) can also be employed, in which case it is not necessary to neutralise the excess of nitric acid. Each 1 c.c. of $N/10$ silver nitrate solution corre-

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[1] *Z. anal. Chem.*, 1893, **32**, 405.

sponds to 0·00585 g. NaCl; a solution containing 2·9054 g. $AgNO_3$ per litre corresponds per 1 c.c. to 0·001 g. NaCl.

7. Sodium sulphate.—Twenty c.c. of the solution are acidified with hydrochloric acid, in not too great excess, heated to boiling, and a hot solution of barium chloride added. Should the bulk of precipitated barium sulphate be small, it may be at once transferred to and washed on the filter with hot water and ignited in a platinum crucible whilst still wet. Each one part $BaSO_4$ corresponds to 0·60885 parts Na_2SO_4.

By taking advantage of the methods of weighing and taring described on p. 20, the gravimetric method of estimation is quite as rapid as the volumetric process (p. 277), and is at the same time appreciably more accurate.

8. Carbonating test.—An average sample of the full charge, taken by mixing together equal quantities of the solutions from each ball tested, is carbonated by a current of carbon dioxide, and filtered. The sum of the Na_2CO_3, Na_2SO_4, and NaCl is then determined by evaporating the filtrate and weighing the dry residue.

2. VAT LIQUOR

The liquor should be as far as possible of a bright yellow colour, and should not be tinged brown or green. The strength should be from 54° to 57° Tw. (sp. gr. 1·26 to 1·28), measured warm. Since a considerable separation of crystals takes place on cooling, the liquor must be examined whilst still warm, and if necessary kept at 40°. It is best, and saves much time, to withdraw small portions (2 to 5 c.c.) in accurate pipettes from the non-diluted liquor for the following tests.

Specific gravity.—The specific gravity is taken by the hydrometer, and, as explained above, necessarily in the warm solution. Lunge[1] has shown that if the temperature of the liquor be taken at the same time a very close approximation to the amount of solid material in the liquor may be obtained since the percentage corresponds almost exactly with the percentage of pure sodium carbonate present in a sodium carbonate solution of the same specific gravity (*cf.* Tables, pp. 448 and 449.

The chemical examination of the vat liquor includes the following determinations:—

1. Sodium carbonate.—Two c.c. are titrated with normal hydrochloric acid. If methyl orange be employed as indicator, the solution is cooled by addition of cold water. The number of c.c. found under 2, together with $\frac{1}{10}$ of the number of c.c. found under 3, must be deducted from the number used in this test.

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[1] *Chem. Ind.*, 1881, 4, 376.

2. **Caustic Soda.**—Two or 5 c.c. are measured off and treated as described on p. 424.

3. **Sodium sulphide.**—This is determined in 2 c.c. of the liquor as described on p. 425. Errors arising from the presence of other sulphur compounds may be neglected.

4. **Sodium sulphate.**—Two c.c. are examined, as on p. 426.

5. **Total Sulphur.**—Five c.c. of the liquor are oxidised by addition of strong bleaching powder solution and hydrochloric acid in excess, taking care that the solution smells strongly of chlorine. The solution is filtered and precipitated by barium chloride.

6. **Sodium chloride.**—Two or 5 c.c. are neutralised as described on p. 425, and titrated.

7. **Sodium ferrocyanide.**—This may be estimated by de Haën's permanganate method, viz., precipitation as Prussian blue, decomposition of this on the filter by sodium hydroxide solution, and titration of the re-formed sodium ferrocyanide by permanganate. The following modification of Hurter's copper sulphate method is, however, both better and quicker. In its original form[1] the method had the disadvantage that the expulsion of the chlorine from the excess of bleach used was a very tedious operation, during which decomposition of the ferrocyanide produced was liable to occur. Lunge and Schäppi[2] have overcome this difficulty by adding only so much bleach solution as is actually necessary for the oxidation. The improved method is carried out as follows. Twenty c.c. of the liquor, or a larger volume in the case of a low cyanide content, are acidified with hydrochloric acid and a strong solution of bleaching powder added from a burette to the well-agitated liquor. A drop of the mixture is withdrawn from time to time and added to a drop of ferric chloride, free from ferrous chloride, on a white plate. The oxidation of ferrocyanide to ferricyanide is complete when the ferric chloride test gives only a brown solution free from Berlin blue. A drop of bleaching powder in excess does not matter, but if too much has been taken or too large a volume of the solution withdrawn for spotting, a fresh portion of the sample is taken and nearly the full quantity of bleach solution required run in at once, only a few tests on the plate being then necessary.

N/10 copper solution (containing 3·180 g. Cu or 12·488 g. crystallised copper sulphate per litre) is then added from a burette to the oxidised liquor, causing precipitation of yellow copper ferricyanide $Cu_3Fe_3(CN)_{12}$. From time to time the solution is tested by mixing a drop of the turbid liquid with a drop of dilute ferrous sulphate solution on a porcelain plate. The addition of the copper solution is continued so long as the test gives the blue colour, due to the interaction of the ferrous sul-

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[1] *Chem. News*, 1879, 39, 25; Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 626.

[2] *Chem. Ind.*, 1881, 4, 370.

phate and sodium ferricyanide, and until the colour produced on the plate has a distinct reddish tinge. When this stage has been reached all the ferricyanide has been converted into the copper compound; the red colour is due to the reduction of the yellow ferricyanide of copper to the red ferrocyanide by the ferrous sulphate. The reaction must be taken as finished as soon as the first marked reddening occurs, even though this disappears after a short time. Each 1 c.c. of the copper solution should correspond to 0·01013 g. $Na_4Fe(CN)_6$; but later work[1] has shown that such is not the case, and that the factor to be used is 0·0123 g. $Na_4Fe(CN)_6$ per 1 c.c. copper solution. It is, however, advisable to check the copper solution by standardising it directly with pure potassium ferrocyanide.

Zulkowsky[2] estimates the ferrocyanide by adding the liquor to a boiling solution of zinc sulphate, acidified with sulphuric acid, until a blue colour is produced at the line of contact when a drop of the solution and a drop of ferric chloride are placed a little distance apart on filter paper. The precipitate has the composition:—

$$K_4Fe(CN)_6 . 3Zn_2Fe(CN)_6 . 12H_2O.$$

Zaloziecki[3] adds zinc carbonate to the solution to be tested, passes carbon dioxide through the hot solution, and titrates a portion of the filtrate with normal acid and methyl orange. The ferrocyanide present in the liquor is calculated from the quantity of sodium carbonate formed according to the equation:—

$$2Na_4Fe(CN)_6 + 4ZnCO_3 = 2Zn_2Fe(CN)_6 + 4Na_2CO_3$$

Should the liquor, as in the case of vat liquor, be alkaline before the addition of the zinc carbonate, the acid corresponding to such alkalinity must be deducted from that used after the above treatment.

Hawliczek[4] estimates the total cyanogen by heating the black ash, placed in a wrought-iron tube, in a current of hydrogen at a red heat. By this treatment the cyanogen is said to be converted quantitatively into ammonia, which is collected in normal acid.

The *thiocyanate* may be determined approximately by Hurter's method, which consists in first precipitating the ferrocyanide by addition of zinc chloride to the acidified liquor, filtering, and then comparing the red coloration, produced on addition of ferric chloride to the filtrate, with a series of standard solutions containing known quantities of thiocyanate and ferric chloride.

8. Silica, Alumina, and Ferric oxide. Parnell's method.[5]—One hundred c.c. of the liquor are treated with an excess of hydrochloric acid, a considerable quantity of ammonium chloride solution added, followed

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[1] *Chem. Ind.*, 1882, **5**, 79.

[2] *Dingl. polyt. J.*, 1883, **249**, 168.

[3] *Z. angew. Chem.*, 1890, **3**, 210 and 301.

[4] *J. Soc. Chem. Ind.*, 1889, **8**, 353.

[5] *Chem. Ind.*, 1880, **3**, 242.

by excess of ammonia, and the solution boiled until all smell of the latter has disappeared. The precipitate settles well, and may be filtered and washed without difficulty. On washing with hot water it acquires a deep blue colour (owing to formation of Prussian blue?). The mixture of SiO_2, Al_2O_3, and Fe_2O_3 is ignited and weighed.

9. **Carbonating Test.**—A considerable volume of the vat liquor is carbonated by passing a current of carbon dioxide through it, and filtered. The filtrate is evaporated to dryness and the residue tested for alkalinity, sodium sulphate, and sodium chloride.

An example of the method of calculating the results and of the practical conclusions to be drawn from the data obtained, is given in Lunge's *Sulphuric Acid and Alkali*, vol. ii., p. 628.

3. CARBONATED LIQUORS

These are examined in the same way as vat liquor. The contained *bicarbonate* is estimated in addition. The estimation of carbonic acid is performed most accurately and quickly by the Lunge and Marchlewski method as modified by Lunge and Rittener[1] (p. 153), which is equally applicable for very large and for very small amounts of carbonic acid. Failing the apparatus necessary for this method, approximate results, sufficiently accurate for all practical purposes, may be obtained as follows.

The carbonated liquor is titrated cold, using phenolphthalein as indicator with $N/5$ hydrochloric acid until the red colour disappears, observing the precautions given on p. 73, especially cooling to nearly 0°. The other conditions, high concentration and a large percentage of sodium chloride, are present at the start and are brought about during the titration respectively. Methyl orange is then added and the titration continued until the change to pink occurs. If a c.c. of $N/5$ hydrochloric acid have been taken for the first titration, and b c.c. for the second, then the number of c.c. corresponding to the constituents of the liquor are: $b-a$ for the bicarbonate, $2a$ for the alkali present as Na_2CO_3, and $a+b$ for the total alkali. The ratio of bicarbonate to carbonate can thus be readily calculated.

Other methods for determining bicarbonate are described under "Bicarbonate" (p. 467).

The mother liquors resulting from the manufacture of soda crystals are examined in the same way as carbonated liquors.

4. SODA MOTHER LIQUORS

Appreciable quantities of sodium sulphite and thiosulphate may occur in these liquors, in addition to sodium sulphide, especially when they are derived from non-carbonated liquors.

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[1] *Z. angew. Chem.*, 1906, **19**, 1849.

The estimation of sulphide-sulphur is generally carried out by expelling the sulphuretted hydrogen with acid and absorbing it by a suitable reagent. The detailed communications of Marchlewski[1] and of Jannasch[2] give full information on this method.

The determination is best made in a flask provided with a tap funnel reaching nearly to the bottom, and with an exit-tube connected with one or two ten-bulb tubes (Fig. 127), filled with ammoniacal hydrogen peroxide, either free from sulphuric acid or in which the quantity of sulphuric acid present is known. The material is introduced into the flask; in the case of a solid it is covered with well-boiled water, and after the air has been expelled from the apparatus by a rapid current of hydrogen, hydrochloric acid, diluted with an equal volume of well-boiled water, is slowly admitted through the funnel. The solution is finally raised to gentle boiling, and hydrogen passed through for fifteen minutes. The contents of the receiving tubes are then heated to boiling to complete the oxidation, acidified with hydrochloric acid, and the sulphur precipitated as barium sulphate. Sodium hydroxide solution, free from sulphate, may be employed instead of the ammoniacal hydrogen peroxide, and the absorbed sulphur gases converted to sulphate by treating the solution with hydrochloric acid and bromine water and boiling until the excess of bromine has been expelled. The hydrogen employed must be washed by an alkaline solution of lead acetate and then with water.

Instead of the above absorbents $N/10$ iodine solution may be employed, the first bulb-tube being filled with this solution, and the second with an equal volume of $N/10$ sodium thiosulphate solution, to catch any iodine carried forward. The two solutions are combined at the end of the experiment, and the excess of thiosulphate determined by titration. The sulphuretted hydrogen corresponding to the iodine taken up is calculated from the equation :—

$$H_2S + I_2 = 2HI + S.$$

The presence of carbonate in the liquors does not interfere in any of these methods, but sulphites and thiosulphates will lead to error, owing to the liberation of sulphur dioxide.

The following method[3] is well adapted to the rapid estimation of *sulphide*, *sulphate*, *sulphite*, and *thiosulphate*, when present together in solution.

1. The sulphate originally present is determined in one portion of the liquor. The air in the flask used for precipitation is first displaced by carbon oxide, to prevent oxidation of the lower sulphur compounds present, the solution heated to boiling, acidified with hydrochloric acid, and the sulphate precipitated by addition of barium chloride.

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[1] *Z. anal. Chem.*, 1893, **32**, 403.

[2] *Z. anorg. Chem.*, 1896, **12**, 124, 134, 158.

[3] Grossmann, *Z. anal. Chem.*, 1889, **28**, 79.

2. A second portion is acidified with acetic acid, diluted with air-free water, and titrated with iodine, using starch as indicator. This gives the $Na_2S+Na_2SO_3+Na_2S_2O_3$.

3. A third portion is treated with cadmium carbonate to remove the sulphide, filtered, the filtrate acidified with acetic acid and titrated with iodine. This gives the Na_2SO_3 and $Na_2S_2O_3$ present. The difference between the readings obtained under 2 and 3 gives the Na_2S.

4. A fourth portion is oxidised by bromine water or bleaching-powder solution (p. 427), and the total sulphate estimated. From the value so obtained, the sulphate found under 1 and the sulphate corresponding to the sulphide present are deducted. If B represents the remaining sulphate, expressed in g. Na_2SO_4, and derived from the sulphite and thiosulphate, and A the total sulphite and thiosulphate found in test 3, the $Na_2S_2O_3$ present $= (0{\cdot}741784\ B-0{\cdot}414698\ A)$ g. and the $Na_2SO_3 = (0{\cdot}661417\ A-0{\cdot}295775)$ g.

Kalmann and Spüller[1] give the following process based on the behaviour of barium sulphite and barium thiosulphate towards water, the former being practically insoluble, whilst the latter is soluble in a large volume of water.

(*a*) The total alkalinity is determined in a measured volume of the solution by titration with normal acid, using methyl orange as indicator. The acid required corresponds to the sum of the sodium carbonate, sodium sulphide, sodium hydroxide, and half of the sodium sulphite present, since Na_2SO_3 reacts alkaline and $NaHSO_3$ neutral towards methyl orange (p. 65).

(*b*) An equal volume of the liquor is acidified with dilute acetic acid and titrated with $N/10$ iodine after the addition of starch solution. The iodine used corresponds to the sum of the sodium sulphide, sodium sulphite, and sodium thiosulphate present.

(*c*) A portion of the solution, double the volume of that employed in each of the tests 1 and 2, is treated with a solution of an alkaline zincate, to precipitate the sulphide, and made up to a definite volume. One-half of this is then filtered off, acidified with acetic acid, and titrated with $N/10$ iodine solution and starch. The iodine used corresponds to the sodium sulphite and sodium thiosulphate.

(*d*) Excess of barium chloride is added to a larger portion of the liquor—three or four times that used in test 1—the solution made up to a definite volume with well-boiled water, the precipitate allowed to settle, and the solution then filtered.

(*α*) One-third or one-quarter of this solution is titrated with normal acid, the volume required corresponding to the sodium hydroxide and sulphide present.

(*β*) A second one-third, or one-quarter, is acidified with acetic acid

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[1] *Dingl. polyt. J.*, 1887, **264**, 456.

and titrated with *N*/10 iodine solution. This gives the sulphide and thiosulphate present.

The calculation is as follows :—

$b - d\beta = A$ c.c. *N*/10 iodine solution, corresponding to the Na_2SO_3
$b - c = B$,, ,, ,, Na_2S
$d\beta - (b - c) = C$,, ,, ,, $Na_2S_2O_3$
$d\alpha - 1/10\ B = D$,, normal acid, ,, $NaOH$
$1 - (d\alpha - 1/20\ A) = E$,, ,, ,, Na_2CO_3

The following method for the estimation of sulphite and thiosulphate, when present together, is due to Kalmann.[1] In the reaction $Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$, acid is produced; in the reaction $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, the solution remains neutral. The test is therefore carried out by allowing the solution to be examined to flow from a burette into a measured volume of iodine solution until this is just decolorised, then adding methyl orange and titrating the acid formed in the iodine titration by *N*/10 sodium hydroxide solution. The iodine equivalent of the sodium hydroxide used gives the sulphite, and the difference between this and the total iodine taken corresponds to the thiosulphate. This method of testing is, of course, only applicable in the absence of carbonate or after any carbonate present has been exactly neutralised, which is not always easily accomplished.

Dobriner and Schranz[2] state that only Na_2S and NaSH, or Na_2S and NaOH, and not all three substances, can exist together in solution, and that this should be taken into account in calculating and stating the results of analysis.

Autenrieth and Windaus[3] separate sulphite and thiosulphate by addition of strontium nitrate, which precipitates the sulphite but leaves the thiosulphate in solution. According to experiments carried out in Lunge's laboratory by Bruhns, the method gives useful if not quite accurate results, and it may therefore be recommended, more especially as it affords a direct separation of the two substances.

Feld[4] describes the following process for estimating sulphur in all stages of oxidation, the method being more particularly intended for liquors containing compounds of the alkali earths. Free sulphur, which may be dissolved in the thiosulphate or polysulphide present in the liquors, is extracted by carbon bisulphide and separated from this solution by distillation. The sulphuretted hydrogen is then driven off by distilling the liquor with magnesium chloride in a current of carbon dioxide (which makes the reaction quantitative) and collected in *N*/10 iodine solution. For this test three absorption vessels are employed; two filled with iodine solution, and the third with *N*/10 thiosulphate

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[1] *Ber.*, 1887, **20**, 568.

[2] *Z. angew. Chem.*, 1896, **9**, 455.

[3] *Z. anal. Chem.*, 1898, **37**, 291.

[4] *Chem. Ind.*, 1898, **21**, 372.

solution to retain any iodine carried forward by the gas. The sulphuretted hydrogen liberated may arise from monosulphide, polysulphide, or sulphydrate. Should polysulphide be present, sulphur separates out during the distillation with magnesium chloride, and is subsequently extracted from the residue by means of carbon bisulphide; should sulphite also be present, a portion of the polysulphide sulphur may combine with this to form thiosulphate. The residual liquor from the distillation is oxidised by the addition of iodine in excess, which liberates sulphur from any sulphide of iron present, according to the equation:—

$$2FeS + 3H_2O + 6I = Fe_2O_3 + 2S + 6HI.$$

The liberated sulphur is extracted with carbon bisulphide as before. The thiosulphate, or rather the resulting tetrathionate, is decomposed by distilling the residue from the previous operation, or a fresh portion oxidised by iodine, with aluminium and hydrochloric acid, and collecting the sulphuretted hydrogen evolved in iodine solution, as above. The conversion of the tetrathionate to sulphuretted hydrogen is quantitative, but additional sulphuretted hydrogen will, of course, be produced from any other polythionates present. Sulphurous acid is estimated by treatment with excess of mercuric chloride, which decomposes all the sulphur compounds with the exception of sulphite, followed by distillation with hydrochloric acid, and collecting the liberated sulphur dioxide in iodine solution.

Browning and Howe[1] dissolve 0·1 g. of the material in 10 or more c.c. of water, add potassium or sodium hydroxide or ammonia solution until the reaction is faintly but distinctly alkaline, then excess of zinc acetate, and filter. The precipitate is examined for sulphide by addition of acid. Acetic acid is added in slight excess to the filtrate, followed by barium chloride, and the solution again filtered through a double filter paper. The filtrate is treated with iodine solution until a distinct yellow colour is produced, and this is removed by the addition of a little stannous chloride and hydrochloric acid. Any precipitation at this stage indicates the presence of sulphite. The filtrate is then treated with bromine water in slight excess, and the excess removed with stannous chloride as above; any precipitate found arises from the presence of thiosulphate in the original liquor.

The following method has been worked out by Lunge and J. H. Smith.[2] The sulphate is determined by displacing the air in the precipitating flask by carbon dioxide, to prevent oxidation, heating the solution, acidifying with hydrochloric acid, and precipitating with barium chloride. A second portion is diluted with air-free water acidified with acetic acid, and titrated with $N/10$ iodine solution. A third portion,

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[1] *Chem. News*, 1898, **78**, 213.

[2] *Chem. Ind.*, 1883, **6**, 301.

four times as large, is treated with zinc acetate or cadmium carbonate to remove the sulphide, made up to a definite volume, allowed to settle, and a quarter of the solution taken for each of the following determinations: (1) iodine equivalent = M; (2) treatment with permanganate solution of strength W (determined according to the equation: $3Na_2S_2O_3 + 8KMnO_4 + H_2O = 3Na_2SO_4 + 3K_2SO_4 + 8MnO_2 + 2KOH$) in considerable excess, and without acidifying. This treatment is carried out by allowing the liquor to flow into the permanganate solution, then adding an acid solution of ferrous sulphate, and finally titrating back the excess of this with permanganate. If the net quantity of permanganate used be called N, the thiosulphate sulphur S, and the sulphite sulphur s, then:—

$$S = 1/7\,(8WN - 0.0064\ M)$$
$$s = 2WN - 2S.$$

The quantity of sulphide present is found by deducting the value M from the figure for the original iodine titration.

This process has been further tested by Lunge and Segaller[1] and found to give exactly the same results as are obtained by the method proposed by Richardson and Aykroyd,[2] who had, through incorrect manipulation, stated that the Lunge-Smith method was inexact. Richardson and Aykroyd estimate the sulphate by precipitating cold with barium chloride after addition of tartaric acid; a second portion is treated with iodine, and the acid produced by interaction with the sulphite, titrated with methyl orange as indicator, exactly as described by Kalmann (p. 422). The sulphide-sulphur is estimated in the ordinary manner.

Dupré and Korn[3] propose to decompose sodium sulphite by boiling with sodium acetate and potassium chlorate in acetic acid solution; the thiosulphate remains unaltered under this treatment. Lunge was unable to obtain satisfactory results by this method.

A very complete summary of the numerous earlier investigations on the action of potassium permanganate on thiosulphate, supplemented by further experiments, has been made by Dobbin,[4] from which he has drawn the following conclusions. When neutral solutions of thiosulphate and permanganate react in the cold, there results a dark brown, flocculent precipitate of variable composition, the solution remaining neutral. The quantity of permanganate necessary to produce a permanent coloration is less than that indicated by theory, assuming the thiosulphate to be oxidised to sulphate, and the permanganate to be reduced to manganese dioxide. The brown precipitate always contains manganese in lower stages of oxidation than MnO_2, in varying quantity, together with traces

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[1] *J. Soc. Chem. Ind.*, 1900, **19**, 221.

[2] *Ibid.*, 1896, **15**, 171.

[3] *Z. angew. Chem.*, 1902, **15**, 225.

[4] *J. Soc. Chem. Ind.*, 1901, **20**, 212.

of sulphur compounds. The solution separated from this precipitate always contains tetrathionate in addition to sulphate, and complete oxidation to sulphate cannot be effected even after prolonged boiling; other sulphur compounds do not appear to be present.

In view of these results, it would appear that the accuracy of all the earlier methods for the separation of the various sulphur compounds must be called into question.

Dobbin confirms the statement, frequently lost sight of, that barium sulphate is not altogether insoluble in the presence of thiosulphate, and that when the latter is present the sulphate determination is inexact.

The total sulphur and total oxidisable sulphur in soda mother liquors are also always estimated (*cf.* p. 436).

5. Vat Waste

Vat or tank waste must always be examined as a check on the lixiviation process, some idea as to the completeness of which can be gauged from the external appearance of the waste.

Thoroughly extracted alkali waste may be recognised as such by its appearance, and analysis is usually in accord with the conclusions formed. It forms a uniform mass, neither slimy nor too coarse, of blue-grey to black-grey colour, and contains very few pieces as large as peas, the greater proportion being of small size. Even the larger pieces should readily yield to pressure. The presence of coarse hard pieces of the size of, or larger than, hazel nuts in the waste indicates poor lixiviation, and points to a considerable loss of soda.

Whatever the appearance of the waste, a chemical examination is essential. If it be not intended to recover the sulphur, an estimation of the available alkali is usually considered sufficient; a test of the total alkali is made in addition from time to time. If the sulphur is to be recovered, the further determinations of oxidisable and total sulphur must always be made, although different methods of testing may be adopted according to the nature of the process in use.

A. *The non-oxidised Alkali Waste.*

One or two samples are taken each day from the heaps of fresh waste, and placed in large, wide-necked, glass-stoppered bottles, the samples being as far as possible representative of the bulk. In the early days of the industry the samples were exposed to the atmosphere until dry, and all estimations were made on the air-dried waste. Working in this way very variable results were obtained, according to the extent of oxidation undergone by the waste. Now the waste is always examined in the moist condition and the results calculated on this basis. The percentage of water may be taken in round figures as 40; it is, however, estimated directly when necessary. The constituents usually estimated are available and total soda, oxidisable and total sulphur.

1. **Available Soda.**—The earlier work of Lunge[1] is now out of date, and Watson's[2] modification of Lunge's method is generally employed.

Twenty g. of the waste are well stirred with from 150 to 200 c.c. of warm water and allowed to stand for one hour; at the end of this time the clear liquor is decanted off and treated for five minutes with a current of carbon dioxide. On passing the gas the solution becomes at first cloudy, but it clears later on as bicarbonate is formed and sulphuretted hydrogen evolved. This affords an indication that the whole of the calcium has been converted into bicarbonate. The solution is then evaporated to half its bulk or less, filtered from calcium carbonate, and the filtrate titrated with normal acid, using methyl orange as indicator. The filtrate still contains calcium compounds, but only in the form of sulphate or other neutral salt, which exerts no appreciable influence. Watson found by this method only 0·025 per cent. of soluble soda as an average of a series of analyses extending over a year.

2. **Total Soda** (including insoluble sodium compounds; Lunge's method).—17·71 g. of waste are heated in a porcelain or iron dish with sulphuric acid of sp. gr. 1·5 until the waste is thoroughly disintegrated and the mixture has been transformed into a stiff paste, when it is evaporated and all free sulphuric acid driven off by heating. Hot water is added to the residue, which is broken up with a wooden spatula and transferred to a 250 c.c. cylinder. Pure milk of lime (prepared from ordinary slaked lime by pouring off the first alkaline aqueous extract) is added to neutralise the free acid and precipitate any magnesia present, the cylinder filled to the 250 c.c. mark and the liquid allowed to settle. Fifty c.c. of the clear solution are pipetted off, treated with 10 c.c. of saturated barium hydroxide solution, filtered through a dry filter paper, and 50 c.c. of the filtrate treated with carbon dioxide till all the baryta is precipitated and, after filtration, titrated with normal acid. Each 1 c.c. of normal acid corresponds to 1 per cent. Na_2O when the above quantities are taken, this factor including allowance for the volume of the waste.

3. **Total Sulphur.**—Two g. of the waste are treated with excess of strong bleaching powder solution and hydrochloric acid, to convert all sulphur to sulphate, the mixture filtered, and the sulphate determined by addition of barium chloride to the filtrate. Care must be taken that the solution smells strongly of chlorine after the oxidation.

4. **Oxidisable Sulphur.**—This is arrived at by difference, by estimating the sulphur originally present as sulphate in the waste and deducting the value so obtained from the total sulphur obtained under test 3. Two

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[1] *Chem. Ind.*, 1881, **4**, 372; *Z. angew. Chem.*, 1890, **3**, 571.

[2] *J. Soc. Chem. Ind.*, 1890, **9**, 1107.

g. of the waste are boiled with hydrochloric acid, filtered, the insoluble matter washed with dilute hydrochloric acid, the filtrate nearly neutralised by addition of pure sodium carbonate and precipitated by barium chloride.

B. *The Chance-Claus Sulphur Recovery Process.*[1]

1. Estimation of Sulphur present as Sulphide.—The apparatus employed consists of a flask fitted with a tap-funnel and gas-exit tube, the latter being connected with an absorption vessel, such as that shown in Fig. 127 (p. 338), charged with a solution of alkali hydroxide and preferably connected with an aspirator. Two g. of the waste and a small quantity of water are introduced into the flask, and hydrochloric acid, diluted with an equal volume of water, gradually run in from the funnel until decomposition is complete. The solution is then boiled to drive off the whole of the gas, much water being carried forward and condensed in the absorption vessel during the operation. When about one-third of the water has been evaporated and the two-thirds remaining in the flask are boiling hot, the funnel tap is opened, the apparatus allowed to cool, and the contents of the absorption vessel transferred to a 500 c.c. flask and made up to this volume. An aliquot part of the solution is taken, diluted considerably with well-boiled water, neutralised with acetic acid, and titrated with $N/10$ iodine solution, each 1 c.c. of which = 0·0016 g. S. (*Cf.* also p. 430 for estimation of sulphide-sulphur.)

2. Sulphur present as Sulphide in Carbonated mud.—Six g. are taken for the analysis, which is otherwise carried out exactly as under test 1.

3. Sulphide-sulphur and Carbonic acid in vat waste.—This estimation is but seldom made. The apparatus required consists of a small flask fitted with a tap-funnel and connected with a U-tube filled with sodium sulphate, to absorb any hydrochloric acid that passes over, and a sufficiently large number of calcium chloride tubes to thoroughly dry the gas. Beyond the drying tubes two potash bulbs are provided and these are in turn connected with a weighed calcium chloride tube. Two g. of the waste together with some water are introduced into the flask and a current of nitrogen then passed through the apparatus. (The nitrogen is best prepared from lime-kiln gas by first washing this by bubbling through sodium hydroxide solution, then passing it through a red-hot tube filled with copper turnings, and finally washing with alkali hydroxide and baryta water.) The waste is decomposed by hydrochloric acid, the solution boiled, and all sulphuretted hydrogen and carbon dioxide carried forward to the absorption tubes by the current of nitrogen, which is continued for a considerable time. The gain in

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[1] *Cf.* Lunge, *Z. angew. Chem.*, 1890, **3**, 573. For a description of the process, see Lunge's *Sulphuric Acid and Alkali*, vol. ii., p. 867.

weight of the potash bulbs and final calcium chloride tube gives the weight of CO_2 and H_2S contained in the waste. The H_2S is estimated by treating the potassium hydroxide solution as described above under test 1, and the CO_2 obtained by taking the difference between the two determinations.

4. **Sulphur present as Sulphide in solutions of calcium sulphide or sodium sulphide.**—Ten c.c. are diluted to 250 c.c., an aliquot part of this diluted with a large volume of air-free water, acidified with acetic acid, and titrated as under 1. Should thiosulphate be present, it is estimated as under 5 and deducted from the total. Should polysulphide be present, only the sulphur liberated as sulphuretted hydrogen and not that precipitated by addition of acid is shown by this method.

5. **Soda, Lime, and Thiosulphate in sulphur liquors.**—The total alkalinity ($CaO + Na_2O$) is determined by titrating 5 c.c. of the liquor with hydrochloric acid, using methyl orange as indicator. A second portion of 50 c.c. is treated with carbon dioxide to drive off all the sulphuretted hydrogen (tested by lead paper), the solution boiled to decompose the calcium bicarbonate, diluted to 50 c.c., allowed to settle, and 50 c.c. of the clear solution titrated as above, the acid required representing the Na_2O present. The CaO is obtained as the difference of the two titrations.

A further portion of the carbonated liquor is titrated for thiosulphate by $N/10$ iodine solution, 1 c.c. of which = 0·006412 g. S as $Na_2S_2O_3$.

The separation of the various sulphur compounds has been described above (p. 430).

6. **Lime-kiln gases.**—The carbon dioxide is estimated in any form of gas burette or in an Orsat apparatus (Fig. 76, p. 199); the latter allows the oxygen to be determined at the same time.

7. **Gas from the Gas-holder.**—(*a*) The sulphuretted hydrogen and carbon dioxide together are estimated as in test 6.

(*b*) The sulphuretted hydrogen is determined in a wide-necked flask of known capacity, say about 500 c.c. The flask is fitted with a double bored rubber stopper through which pass two glass tubes, the one reaching nearly to the bottom of the flask, and the second ending just below the stopper. Both tubes are provided with taps outside the flask. The gas to be examined is passed through the flask until all air has been expelled; 20 or 25 c.c. of normal sodium hydroxide solution are then admitted through one of the taps, and after thorough shaking the liquor is poured off, the flask well washed out, and the liquor and washings made up to a known volume. An aliquot part of the solution is then diluted with a large volume of air-free water, acidified with acetic acid and titrated with iodine. It is advisable to use an iodine solution containing 11·46 g. I per litre, since 1 c.c. of such a solution corresponds to 1 c.c. H_2S measured at 0° and 760 mm. pressure.

Lunge and Rittener's method (*cf.* pp. 153 and 514) can also be applied to the analysis of mixtures of carbon dioxide and sulphuretted hydrogen. The two gases are absorbed together by sodium hydroxide, and an aliquot part of the sample then transferred to a second burette and absorbed with $N/10$ iodine solution, the excess of which is titrated back after the absorption.

8. **Exit Gases from the Claus kiln.**—These gases contain small amounts of sulphuretted hydrogen and sulphur dioxide, both of which compounds by interaction with iodine solution give rise to two molecules of hydriodic acid for each atom of sulphur present; but whilst the sulphuretted hydrogen does not cause any further increase in the acidity, the sulphur dioxide gives rise to an equivalent of sulphuric acid. The sum of the H_2S+SO_2 is consequently measured by estimating the quantity of iodine converted into hydriodic acid, and the sulphur dioxide by the determination of the acidity remaining after the hydriodic acid thus formed has been neutralised. Since, however, the passage of a large volume of gas through iodine solution volatilises a portion of the iodine, it is necessary to insert a flask containing sodium hydroxide or, preferably, sodium thiosulphate solution. One or more litres of the gas are aspirated through 50 c.c. of $N/10$ iodine solution contained in a bulb-tube (Fig. 127, p. 338), followed by a similar tube filled with 50 c.c. of $N/10$ sodium thiosulphate solution. When the operation is finished, the contents of the two tubes are emptied into a beaker and titrated with $N/10$ iodine solution and starch; the number of c.c. required $(=n)$ multiplied by 0·001603 gives the total sulphur present as SO_2+H_2S. The blue coloration is then removed by addition of a drop of thiosulphate solution, methyl orange added, and the solution titrated with $N/10$ sodium hydroxide. If the number of c.c. necessary to neutralise the solution be called m, then $(m-n)\times{\cdot}001603$ gives the quantity of sulphur present as SO_2.

II. THE AMMONIA-SODA PROCESS

RAW MATERIALS

1. **Rock-salt and Brine** (*cf.* p. 397 *et seq.*).

2. **Gas liquor, Ammonium sulphate, and other Ammonium salts** are treated of in Vol. II., under the section "Ammonia," and are examined as there described.

3. **Limestone** (*cf.* p. 481).

4. **Quicklime** is analysed as described under Bleaching powder, p. 483.

5. **Coal**
6. **Coke** } (*cf.* p. 241 *et seq.*, and p. 420).

CONTROL OF WORKING CONDITIONS

1. Ammoniacal Brine.

(*a*) *Sodium chloride.* The solution is acidified by nitric acid, and the sodium chloride estimated by Volhard's method (p. 123), or by titration in the neutral or faintly alkaline solution as described on pp. 123 and 401.

(*b*) *Free and combined Ammonia.* Ten c.c. of the solution are diluted to about 100 c.c. with water and boiled in a distilling flask until all free ammonia and ammonium carbonate have been driven off. The evolved gases are collected in a measured volume of normal hydrochloric acid, the excess of which is determined by titration. When this has been done sodium hydroxide solution is added to the residue in the distilling flask and the distillation continued until all the combined ammonia has been liberated and absorbed in normal acid as above.

2. Bicarbonate vessels (Carbonators). — Free and combined ammonia are determined as under 1.

3. Mother liquors.

(*a*) *Free and combined Ammonia*, as above.

(*b*) *Unchanged Sodium chloride.* Ten c.c. are evaporated in a platinum dish, the residue ignited to drive off all ammonium chloride, and weighed.

4. Bicarbonate.

(*a*) *Total Alkalinity* (*cf.* p. 61 *et seq.*).

(*b*) *Carbonic acid* (*cf.* p. 429 *et seq.*).

(*c*) *Moisture*, determined by ignition, the carbonic acid found under (*b*), and the corresponding water from bicarbonate being deducted.

5. Ammonia distillation.

(*a*) *Free and combined Ammonia*, in the mother liquor, as above, under 1 (*b*).

(*b*) *Milk of Lime*, as under Bleaching powder, p. 484.

(*c*) *Excess of Lime in the stills.* One hundred c.c. are boiled until all the ammonia has been driven off, ammonium sulphate is then added and the boiling continued. The ammonia so liberated corresponds to the excess of lime present; it is absorbed in normal acid, and titrated.

6. Lime-kiln gas.—Estimation of carbon dioxide (*cf.* p. 438).

7. Analysis of the Finished product, as described under "Finished Soda Products," p. 446.

III. MANUFACTURE OF CAUSTIC SODA

The methods described are restricted to those relating to the manufacture of caustic soda by the lime process; the methods involved in the Löwig process (causticising by ferric oxide), follow naturally from the former. The analysis of the liquors obtained in the electrolytic processes are referred to on p. 442.

A. CAUSTICISED LIQUOR

This liquor is examined in the same way as the vat liquors of the Leblanc process (p. 426 *et seq.*); as a rule, only the specific gravity, total alkalinity, sodium carbonate, and sulphur compounds are estimated. A table showing the percentage of sodium hydroxide corresponding to various specific gravities is given under "Caustic Soda," p. 464.

B. FISHED SALTS

The fished salts from the strong liquors consist essentially of monohydrated sodium carbonate and anhydrous sulphate; those fished from weaker liquors contain the same two salts in the hydrated condition.

For analysis, 50 g. of the salts are dissolved in water and made up to 1000 c.c.

1. **Total Alkalinity** is determined in 20 c.c. of the solution, exactly as in the case of caustic soda.

2. **Sodium chloride.**—Twenty c.c. are treated with nitric acid in excess, boiled to decompose the sulphur compounds, and filtered if necessary; after neutralising the excess of nitric acid with sodium carbonate, the solution is titrated with silver nitrate solution as described on pp. 123 and 401.

3. **Sodium sulphate.**—Twenty c.c. are acidified with hydrochloric acid, and hot barium chloride solution added to the boiling solution.

4. **Sodium sulphate from oxidisable sulphur compounds** (sodium sulphite and thiosulphate).—Twenty c.c. of the solution are treated with bleaching powder solution in excess, followed by hydrochloric acid, until the solution acquires an acid reaction and smells distinctly of chlorine (*cf.* p. 427). Barium chloride is then added and the precipitated barium sulphate collected and weighed. From the weight so obtained the weight of barium sulphate obtained in test 3 must be deducted.

C. CAUSTIC "BOTTOMS"

Caustic bottoms are examined for insoluble matter, total alkalinity, and sodium carbonate.

1. **Insoluble matter.**—Twenty g. of the sample are dissolved in water, and the solution filtered into a 500 c.c. flask. The insoluble matter is well washed, burnt whilst still moist in a platinum crucible, ignited, and weighed.

2. **Total Alkalinity.**—Fifty c.c. of the above solution are titrated

hot with normal hydrochloric acid, using phenolphthalein as indicator. Methyl orange is not suitable in this case, owing to the presence of alumina, the quantity of which may amount to from 2 to 3 per cent.[1]

3. **Sodium carbonate** is estimated as described under Caustic Soda (p. 466).

D. LIME MUD

The lime mud is examined for sodium hydroxide and sodium carbonate, free lime, and calcium carbonate.

1. **Total Soda.**—Ammonium carbonate is added to the mud and the mixture evaporated to dryness to decompose all insoluble sodium compounds. The operation is repeated, the whole of the ammonium carbonate driven off, the residue washed with hot water, filtered, and the filtrate titrated for alkalinity. The result is best expressed in terms of Na_2O (0·03105 g. per 1 c.c. normal acid), although the sodium found may originally have been present, partly as hydroxide and partly as carbonate.

2. **Caustic Lime.**—The mud is titrated with normal hydrochloric acid, employing phenolphthalein as indicator, as described on pp. 72 and 423. From the result obtained, the value found under test 1, so far as this represents sodium hydroxide, must be deducted; no appreciable error will be introduced if the amount to be deducted is assumed as equal to half the value found under 1.

3. **Calcium carbonate.**—The total calcium is determined by titrating with acid and methyl orange or litmus and the caustic lime found under test 2 deducted from the total.

IV. ELECTROLYTIC ALKALI LIQUORS

It is scarcely necessary to state that the methods of analysis are the same, so far as the works tests are concerned, for both potash and soda solutions. In the case of potassium compounds a determination of the potassium in the finished product should, of course, be made; for this purpose the methods described in the section "Potassium Salts" (p. 520) are applicable. For the sake of simplicity the expressions sodium carbonate, caustic soda, sodium chloride, etc., are to be taken to include the corresponding potassium compounds, in cases where potassium compounds form the raw materials.

The essential products found in the liquors produced in the electrolysis of sodium chloride are:—sodium hydroxide, sodium carbonate, sodium chloride, sodium hypochlorite, and sodium chlorate.

These are the same as those found in "Eau de Javel," the com-

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[1] Lunge, *Z. angew. Chem.*, 1890, 3, 300.

mercial bleaching solution in which sodium is the basis; the proportions are, however, quite different in the two cases. The same methods of analysis are, however, applicable in both instances; these are given in the section dealing with Bleaching compounds (p. 509).

V. CRUDE FUSED SODA OF THE CELLULOSE INDUSTRY

Under this name[1] is understood the product which results when the waste alkaline liquors obtained in the manufacture of cellulose from wood or straw by the "sulphite process" are, after addition of sodium sulphate, evaporated to dryness and calcined. The product consists essentially of carbonate, hydroxide, silicate, sulphide, sulphite and sulphate of sodium, but contains, in addition to these, small amounts of sodium chloride, iron oxide, lime, magnesia, and alumina. Since these latter substances are without influence on the process, the amount present is seldom estimated. A correct knowledge of the composition of the crude fused soda (recovered soda) is essential to the proper carrying out of the boiling operation, and indicates which constituents are to be removed and which to be added for successful working. In the early days of the process this recovered soda was examined in the same way as Leblanc black ash. Viewed from a purely qualitative standpoint the two materials correspond fairly well, though, from a quantitative aspect, the ratio of the various constituents differs considerably in the two cases. As is well known, the solution obtained on lixiviating black ash consists in the main of sodium carbonate together with a fair proportion of sodium hydroxide, a little sulphate, very little sulphide and still less sulphite, silicate, and aluminate; the cyanogen compounds, etc., may be left out of account in this connection. The crude fused soda, on the other hand, contains very large quantities of sulphide and also marked quantities of silicate, especially in cases where straw has been treated.

The methods employed for the estimation of the extremely small percentages of sulphide and silicate present in Leblanc liquors, although sufficiently exact for such purposes, are not directly applicable to the analysis of the wood-pulp product and, as Lunge and Lohöfer[2] have shown, may easily lead to wholly unreliable results. A consideration of special importance is the fact that the separation of carbonate and hydroxide by means of barium chloride is quite impossible in the presence of silicate; thus from a solution of sodium metasilicate only a portion of the silica (50-60 per cent.) is precipitated, even in the presence of a

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[1] Cf. *Z. angew. Chem.*, 1901, **14**, 1102; *J. Soc. Chem. Ind*, 1901, **20**, 1231.

[2] *Z. angew. Chem.*, 1901 **14**, 1125; *J. Soc. Chem. Ind.*, 1902, **21**, 70.

very large excess of the reagent. As the result of their investigations, Lunge and Lohöfer recommend the following method for determining the chief constituents of crude fused sodium carbonate.

Fifty g. of the average sample are dissolved by continued shaking with 500 c.c. of water free from air and carbon dioxide. Solution is effected in a litre flask at a temperature of 45°, and the solution is diluted to 1000 c.c. before taking portions for analysis.

1. **Insoluble matter** is estimated in the usual manner, as described under black ash.

2. **Alkalinity.**—Twenty c.c. = 1 g. substance are titrated with normal hydrochloric acid and phenolphthalein till the solution becomes colourless, when methyl orange is added and the titration continued until the change to red takes place. The number of c.c. required for each of these stages is noted. The titration must be carried out in the cold solution, and the best results are obtained if the temperature is not much higher than 0° C. (*cf.* pp. 73 and 429). The solution, which is originally colourless, assumes a very faint yellow tinge when the colour change with phenolphthalein is reached; on further addition of acid the solution becomes strongly yellow and milky sulphur is deposited. The colour change with methyl orange is nevertheless quite distinct.

3. **Sulphide and Sulphite.**—Twenty c.c. = 1 g. substance are diluted to about 200 c.c. with air-free water, acidified with acetic acid and rapidly titrated with $N/10$ iodine solution, using starch paste as indicator. The sulphide present is found by deducting from the value so obtained the equivalent of the sulphite found under 4.

As there is a risk of loss of sulphuretted hydrogen when the titration is carried out in an acidified solution, Conroy[1] recommends adding the sulphide liquor to a measured volume of an acidified $N/10$ iodine solution, either until the latter is decolorised, or to use an excess of iodine solution and titrate back with sodium thiosulphate.

4. **Sulphite.**—The sulphide present is precipitated by adding a solution of sodium zincate (prepared by adding sodium hydroxide solution to a solution of zinc acetate until the precipitate first formed goes into solution) to 100 c.c. of the solution, the whole made up to 250 c.c. and filtered through a dry filter paper. Fifty c.c. of the filtrate (= 1 g. substance) are acidified with acetic acid and titrated as above with $N/10$ iodine solution and starch, the iodine required corresponding to the sulphite present.

5. **Silicate.**—Twenty c.c. of the solution are treated with excess of hydrochloric acid, evaporated to dryness, and the silica estimated gravimetrically in the usual way. One part $SiO_2 = 2{\cdot}028$ parts Na_2SiO_3. It is best to add the hydrochloric acid in an atmosphere of carbon dioxide,

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[1] Private communication.

excluding air as far as possible, so that the filtrate from the silica may be available for the estimation of sulphate. These precautions are necessary to prevent oxidation of the sulphuretted hydrogen and sulphur dioxide.

6. **Sulphate** is estimated as barium sulphate by the addition of barium chloride to the acidified filtrate from the silica determination. This method is only exact provided all oxidation has been excluded during the addition of the hydrochloric acid in estimation 5. Further, incorrect results are obtained when relatively large quantities of thiosulphate[1] are present, but this point has little bearing in the analysis of wood-pulp soda, as thiosulphate is not likely to be present in the fresh material.

The calculation of the quantities of the various constituents present is very tedious, and occupies considerable time, if the results of the titrations are each calculated directly to parts by weight of the individual constituents. It is much easier to arrive at the results by comparing the equivalents of the normal solutions employed, as will be evident from the following example of an actual analysis :—

1. Insoluble matter.

(*a*) 10.0039 g. substance gave 1.0836 g. residue.
(*b*) 10.0000 g. ,, 1.0805 g. ,,

Weight of Ignited Residue.

(*a*) 1.0000 g., thus giving 0.0836 g. carbonaceous matter.
(*b*) 0.9904 g., ,, 0.0901 g. ,,

2. Alkalinity in c.c. $N/5$ HCl.

With phenolphthalein, 49.39 ; 49.33 ; mean, 49.36 c.c.
,, methyl orange, 76.74 ; 76.74 ; mean, 76.74 c.c.

3. $Na_2S + Na_2SO_3$.

$$\left.\begin{array}{l}40.23 \text{ c.c. } N/10 \text{ I} \\ 40.27 \text{ c.c. } N/10 \text{ I}\end{array}\right\} \text{Mean, } 40.25 \text{ c.c. } N/10 \text{ I.}$$

4. Na_2SO_3.

$$\left.\begin{array}{l}0.40 \text{ c.c. } N/10 \text{ I} \\ 0.40 \text{ c.c. } N/10 \text{ I}\end{array}\right\} \text{Mean, } 0.40 \text{ c.c. } N/10 \text{ I.}$$

5. Na_2SiO_3.

$$\left.\begin{array}{l}0.0699 \text{ g. } SiO_2 \\ 0.0701 \text{ g. } SiO_2\end{array}\right\} \text{Mean, } 0.0700 \text{ g. } SiO_2.$$

6. Na_2SO_4.

$$\left.\begin{array}{l}0.0536 \text{ g. } BaSO_4 \\ 0.0534 \text{ g. } BaSO_4\end{array}\right\} \text{Mean, } 0.0535 \text{ g. } BaSO_4.$$

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[1] *Cf.* Richardson and Aykroyd, *J. Soc. Chem. Ind.*, 1896, 15, 171 ; *Annual Report on Alkali, etc., Works*, 1899, p. 47 ; also, Dobbin, *J. Soc. Chem. Ind.*, 1891, **10**, 218.

Calculation.

1 c.c. $N/5$ HCl corresponds to 0.0106 g. Na_2CO_3 and to 0.0080 g. NaOH.
1 c.c. $N/10$ I ,, 0.0039 g. Na_2S ,, 0.0063 g. Na_2SO_3.
1 g. SiO_2 ,, 2.028 g. Na_2SiO_3.
1 g. Na_2SiO_3 ,, 81.63 c.c. $N/5$ HCl.
1 g. $BaSO_4$,, 0.6089 g. Na_2SO_4.

The 76.74 c.c. $N/5$ HCl with methyl orange correspond to the :—

$$Na_2CO_3 + NaOH + Na_2SiO_3 + Na_2S + 1/2\ Na_2SO_3 \text{ present.}$$

The 49.36 c.c. $N/5$ HCl with phenolphthalein correspond to the :—

$$NaOH + Na_2SiO_3 + 1/2\ Na_2S + 1/2\ Na_2CO_3 \text{ present.}$$

$$[76.74 - 0.10 (\text{for } 1/2\ Na_2SO_3)] - 49.36 = 27.28 \text{ c.c. } N/5 \text{ HCl.}$$

$$2 \times 27.28 = 54.56 \text{ c.c. } N/5 \text{ HCl} = Na_2S + Na_2CO_3.$$

$$40.25 \text{ c.c. } N/10 \text{ I} = Na_2S + Na_2SO_3.$$

$$40.25 - 0.40 = 39.85 \text{ c.c. } N/10 \text{ I} = Na_2S.$$

$$0.40 \text{ c.c } N/10 \text{ I} = Na_2SO_3.$$

$$54.56 - \frac{39.85}{2} = 34.64 \text{ c.c. } N/5 \text{ HCl} = Na_2CO_3.$$

$$49.36 - 27.28 = 22.08 \text{ c.c. } N/5 \text{ HCl} = NaOH + Na_2SiO_3.$$

1 g. substance, therefore, contains :—

Na_2CO_3 = 34.64×0.0106 = 0.3672 g.
Na_2SiO_3 = 0.0700×2.028 = 0.1420 g.
(= 11.59 c.c. $N/5$ HCl)
NaOH = $(22.08 - 11.59) \times 0.008$ = 0.0839 g.
Na_2S = 39.95×0.0039 = 0.1554 g.
Na_2SO_3 = 0.40×0.0063 = 0.0025 g.
Na_2SO_4 = 0.0535×0.6089 = 0.0326 g.
Insoluble matter = Residue ÷ 10 = 0.1081 g.
(of which the carbonaceous matter = 0.0086 g.)

VI. FINISHED PRODUCTS OF THE SODA INDUSTRY

The various products of the manufacture are : soda ash, soda crystals, crystal carbonate, caustic soda, and bicarbonate, together with an intermediate product known as caustic ash ; the method of analysis of the last does not call for special comment.

The individual products vary somewhat in their properties according to the method of manufacture followed in their preparation. Thus, for example, a non-carbonated ash made by the Leblanc process may contain both caustic soda and sodium sulphide whilst the presence of these compounds is practically impossible in the product of the ammonia-soda process. The chief impurity of Leblanc soda, according to percentage, is sodium sulphate, whilst in ammonia-soda the chief impurity is chloride. Commercial bicarbonate prepared by the ammonia-soda process may contain a small percentage of ammonia, whilst in bicarbonate prepared from soda crystals, ammonia is never present. Generally speaking, however, the same methods are adopted for the examination of any individual product, irrespective of its origin. Any special characteristics of importance dependent on the process of manufacture will be referred to in the description of the methods of analysis employed.

Special attention should be paid to the methods of sampling given on p. 13.

A. SODA ASH

This product consists essentially of sodium carbonate, but it may contain as impurity, small quantities of other sodium salts together with alumina, ferric oxide, water, etc.

Chemically pure sodium carbonate[1] contains 58·53 per cent. Na_2O, and 41·47 per cent. CO_2, and has a specific gravity of 2·5. Various values have been found for the melting-point by different observers; Carnelly gives 814°, le Chatelier 810°, Victor Meyer 849°; the earlier determination of 1098°, due to Victor Meyer and Riddle, has been shown to be incorrect. On fusion, a small quantity of sodium oxide is formed, and at a yellow heat the loss of carbon dioxide may rise to $1\frac{1}{2}$ per cent. This loss on heating is inconsiderable at temperatures below the melting-point and may be altogether obviated by heating in a current of carbon dioxide. No loss occurs below a temperature of 300° (*cf.* p. 85).

The first of the following tables gives the percentage content corresponding to the various specific gravities of solutions of pure sodium

1. Specific Gravity of Solutions of Sodium Carbonate at 15° C. = 60° F.

Specific Gravity.	Percentage by Weight.		Kilos per 1 cubic metre.	
	Na_2CO_3.	$Na_2CO_3\ 10H_2O$.	Na_2CO_3.	$Na_2CO_3\ 10H_2O$.
1·007	0·67	1·807	6·8	18·2
1·014	1·33	3·587	13·5	36·4
1·022	2·09	5·637	21·4	57·6
1·029	2·76	7·444	28·4	76·6
1·036	3·43	9·251	35·5	95·8
1·045	4·29	11·570	44·8	120·9
1·052	4·94	13·323	52·0	140·2
1·060	5·71	15·400	60·5	163·2
1·067	6·37	17·180	68·0	183·3
1·075	7·12	19·203	76·5	206·4
1·083	7·88	21·252	85·3	230·2
1·091	8·62	23·248	94·0	253·6
1·100	9·43	25·432	103·7	279·8
1·108	10·19	27·482	112·9	304·5
1·116	10·95	29·532	122·2	329·6
1·125	11·81	31·851	132·9	358·3
1·134	12·61	34·009	143·0	385·7
1·142	13·16	35·493	150·3	405·3
1·152	14·24	38·405	164·1	442·4

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[1] For further details, *cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 43.

carbonate, together with the corresponding percentage of decahydrated sodium carbonate, and the weight of sodium carbonate, anhydrous and hydrated, contained in 1 cubic metre of solution at 15° C. The data (at 15°) are calculated by Lunge from Gerlach's determinations. The second table gives corresponding data for degrees Twaddell, the percentage content of Na_2O and of Na_2CO_3, and the content of these per cubic foot of solution. The third table (at 30°) is based on Lunge's own determinations, and deals with the stronger liquors which frequently occur in practice and which can only exist above the ordinary atmospheric temperature.

2. Specific Gravity of Solutions of Sodium Carbonate in degrees Twaddell at 15° C. = 60° F.

Twaddell.	Percentage by Weight.		Lbs. per 1 cubic foot of solution.	
	Na_2O.	Na_2CO_3.	Na_2O.	Na_2CO_3.
1	0·28	0·47	0·172	0·294
2	0·56	0·95	0·350	0·598
3	0·84	1·42	0·525	0·898
4	1·11	1·90	0·707	1·209
5	1·39	2·38	0·889	1·521
6	1·67	2·85	1·070	1·830
7	1·95	3·33	1·257	2·149
8	2·22	3·80	1·441	2·464
9	2·50	4·28	1·631	2·788
10	2·78	4·76	1·852	3·116
11	3·06	5·23	2·012	3·440
12	3·34	5·71	2·206	3·772
13	3·61	6·17	2·396	4·097
14	3·88	6·64	2·591	4·430
15	4·16	7·10	2·783	4·759
16	4·42	7·57	2·981	5·098
17	4·70	8·04	3·181	5·439
18	4·97	8·51	3·382	5·783
19	5·24	8·97	3·582	6·125
20	5·52	9·43	3·783	6·468
21	5·79	9·90	3·989	6·821
22	6·06	10·37	4·197	7·177
23	6·33	10·83	4·403	7·529
24	6·61	11·30	4·615	7·891
25	6·88	11·76	4·825	8·249
26	7·15	12·23	5·040	8·617
27	7·42	12·70	5·256	8·988
28	7·70	13·16	5·465	9·354
29	7·97	13·63	5·691	9·713
30	8·24	14·09	5·908	10·103

According to Lunge,[1] these tables not only give the percentage of Na_2CO_3 in solutions of pure sodium carbonate, but they give with

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[1] *Chem. Ind.*, 1881, 4, 376.

almost equal accuracy the percentage of solid matter, that is, sodium carbonate plus impurities, in ordinary vat liquor (*cf.* p. 426).

3. Specific Gravity of Concentrated Solutions of Sodium Carbonate at 30° C. = 86° F.

Specific Gravity at 30°.	Degrees Twaddell.	100-lbs. contain lbs.		1 litre contains grms.	
		Na_2CO_3.	Na_2CO_3, 10 aq.	Na_2CO_3.	Na_2CO_3, 10 aq.
1·310	62	28·13	75·91	368·5	994·5
1·300	60	27·30	73·67	354·9	957·4
1·290	58	26·46	71·40	341·3	921·0
1·280	56	25·62	69·11	327·9	884·7
1·270	54	24·78	66·86	314·7	849·2
1·260	52	23·93	64·59	301·5	813·2
1·250	50	23·08	62·15	288·5	778·5
1·240	48	22·21	59·94	275·4	743·0
1·230	46	21·33	57·55	262·3	707·8
1·220	44	20·47	55·29	249·7	673·8
1·210	42	19·61	52·91	237·3	640·3
1·200	40	18·76	50·62	225·1	607·4
1·190	38	17·90	48·31	214·0	577·5
1·180	36	17·04	45·97	201·1	542·6
1·170	34	16·18	43·38	189·3	510·9
1·160	32	15·32	41·34	177·7	479·5
1·150	30	14·47	39·04	164·4	449·0
1·140	28	13·62	36·75	155·3	419·0

A table showing the influence of temperature from 0° to 100° on the specific gravity of sodium carbonate solutions has been published by Lunge.[1] Liebig[2] has made use of Lunge's figures in calculating the mean values given in the table below.

4. Influence of Temperature on the Specific Gravity of Sodium Carbonate Solutions.

(Approximate mean values for ± 1° C.)

For Temperatures from					For Specific Gravities		
0° to 30°.	30° to 40°.	40° to 50°.	50° to 70°.	70° to 100°.	From	To	
0·0002	0·0004	0·0004	0·0005	0·0005	1·010	1·050	at 15°
0·0003	0·0004	0·0004	0·0006	0·0005	1·060	1·070	
0·0004	0·0004	0·0004	0·0006	0·0006	1·080	1·110	
0·0004	0·0004	0·0005	0·0006	0·0006	1·120	1·170	
0·0004	0·0004	0·0006	0·0007	0·0007	1·180	1·200	
0·0005	0·0004	0·0005	0·0007	0·0007	1·210	1·240	
...	0·0005	0·0005	0·0007	0·0007	1·241	1·252	at 30°
...	0·0005	0·0005	0·0006	0·0008	1·263	1·285	

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[1] *Alkali Makers' Handbook*, p. 136.

[2] Post, *Chem. tech. Analyse*, 2nd edition, vol. i., p. 795.

A very thorough investigation of the specific gravities of solutions of sodium carbonate and of sodium hydroxide has been published by R. Wegscheider and H. Walter;[1] the results differ but slightly from the figures given above up to the third decimal place.

The chemical analysis of commercial soda ash is generally confined to the determination of the available alkali or alkalimetrical degree; a complete analysis is, however, made from time to time as a check upon the process.

Estimation of the available Alkali of Soda ash.—The method generally used is as follows: 26·50 g. of soda ash are weighed off in a small beaker and dissolved by boiling with water in a larger vessel. The solution, together with the small amount of insoluble matter, is transferred to a 500 c.c. flask, made up to this volume, well shaken and filtered, if necessary, through a pleated filter paper covered by a watch-glass. Fifty c.c. of the filtrate are then titrated with normal hydrochloric acid and methyl orange. For an ash containing 98 per cent. Na_2CO_3, 49 c.c. of normal acid (1 c.c. = 2 per cent.) will be required for the titration.

In the method adopted by the German alkali manufacturers, the ash is always ignited before determining the percentage of alkali and the results calculated on the ignited material; this gives the only satisfactory results. 2·6525 g. are taken for the analysis, dissolved in water, and the solution titrated directly without filtering. Each 1 c.c. of normal acid corresponds to 2 per cent. Na_2CO_3.

If the readings are made to $\frac{1}{40}$ c.c. in a 50 c.c. burette graduated in $\frac{1}{10}$ c.c., as may very readily be done in the manner described on p. 49, the error in the reading will not exceed 0·05 per cent. Na_2CO_3.

A normal solution of hydrochloric acid is employed, containing 36·46 g. HCl per litre, standardised both by means of chemically pure sodium carbonate and by silver nitrate (*cf.* p. 83). Litmus solution or phenolphthalein may be used as indicator, but in each case prolonged boiling is necessary; it is much more convenient and accurate to titrate cold, with methyl orange as indicator (*cf.* pp. 60 and 65).

It will be noted that in the method generally adopted here, the alkalinity is determined in the solution only, whilst in the German method the alkalinity due to calcium carbonate, magnesium carbonate, ferric oxide, etc., in the insoluble matter is included in the total. This does not, however, cause any appreciable difference, at all events in the case of ammonia-soda, in which the total insoluble matter (inclusive of sand, carbonaceous matter, and other substances not affecting the alkalinity) does not exceed $\frac{1}{4}$ per cent.

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[1] *Monatsh.*, 1905, **26**, 685; 1906, **27**, 13.

As the whole of the weighed substance is titrated directly in the German method, any error due to relative inaccuracy in the content of the pipette and measuring flask is avoided.[1]

Various methods are in vogue of stating the results of the titration, *i.e.* the strength of the ash. In the scale proposed by Gay-Lussac, the strength is expressed in terms of available soda, under which all the substances present which react with normal acid, such as carbonate, hydroxide, silicate, and aluminate, are included. Chemically pure sodium carbonate contains 58·53 per cent. Na_2O, and would thus correspond to 58·53 degrees Gay-Lussac. These degrees are generally referred to as "English" or "Newcastle degrees," which, however, give the commercial strength always higher than the real value, as the former is based on the assumption that the chemical equivalent of Na_2CO_3 is 54, instead of the true value, 53·05. That is, the commercial percentage of Na_2O is higher than the actual percentage in the ratio of 31·4 to 31. A scale known as the "Liverpool test" was formerly in use in Lancashire; it was an altogether erroneous method of statement, and is hardly ever employed now.[2]

In Germany, the "degrees" indicate percentage of Na_2CO_3, which is rational as applied to sodium carbonate itself; but the scale is also applied to all other sodium compounds, such as caustic soda, which act upon the test acid, and the strength is accordingly quoted in terms of a substance which occurs only as an impurity in the caustic alkali. The scale is, however, in general use commercially.

In France and Belgium, soda compounds of all kinds (also potash, baryta, etc.) are quoted on a basis similar to Gay-Lussac degrees, that is, according to their titrimetric value, leaving out, however, all reference to the particular alkali, whether sodium hydroxide, sodium carbonate, or potassium carbonate. The scale employed is that of Descroizilles, and the degrees indicate the quantity of sulphuric acid monohydrate (H_2SO_4) neutralised by 100 parts of the alkali examined. Since 10 parts of chemically pure sodium carbonate are equivalent to 9·245 parts H_2SO_4, the standard acid is prepared in such a way that 92·45 half cubic centimetres (so-called "divisions") will exactly neutralise 5 g. of pure sodium carbonate; or, in other words, the standard acid contains exactly 100 g. H_2SO_4 to the litre. The "Descroizilles sulphuric acid" is prepared by adding about 3150 c.c. of concentrated sulphuric acid to 50 litres of water, and standardising, as described on p. 86.

The following table (p. 452) shows the relationship between the English, German, and French degrees, and is applicable to sodium hydroxide and all soda products.

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 100; also under "Insoluble Matter" in this section (p. 455).

[2] *Ibid.*, p. 105, and vol. iii., p. 819.

English, German, and French Commercial Alkalimetric Degrees.

Real Soda, Na_2O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na_2CO_3.	French Degrees (Descroizilles).	Real Soda, Na_2O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na_2CO_3.	French Degrees (Descroizilles).	Real Soda, Na_2O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na_2CO_3.	French Degrees (Descroizilles).
0·5	0·51	0·85	0·79	26·5	26·85	45·31	41·88	52·5	53·19	89·76	82·98
1	1·01	1·81	1·58	27	27·35	46·17	42·67	53	53·70	90·61	83·77
1·5	1·52	2·56	2·37	27·5	27·86	47·02	43·46	53·5	54·20	91·47	84·56
2	2·03	3·42	3·16	28	28·36	47·88	44·25	54	54·71	92·32	85·35
2·5	2·54	4·27	3·95	28·5	28·87	48·73	45·04	54·5	55·22	93·18	86·14
3	3·04	5·13	4·74	29	29·38	49·59	45·83	55	55·72	94·03	86·93
3·5	3·55	5·98	5·53	29·5	29·89	50·44	46·62	55·5	56·23	94·89	87·72
4	4·05	6·84	6·32	30	30·39	51·29	47·42	56	56·74	95·74	88·52
4·5	4·56	7·69	7·11	30·5	30·90	52·14	48·21	56·5	57·24	96·60	89·31
5	5·06	8·55	7·90	31	31·41	53·00	49·00	57	57·75	97·45	90·10
5·5	5·57	9·40	8·69	31·5	31·91	53·85	49·79	57·5	58·26	98·31	90·89
6	6·08	10·26	9·48	32	32·42	54·71	50·88	58	58·76	99·16	91·68
6·5	6·59	11·11	10·27	32·5	32·92	55·56	51·37	58·5	59·27	100·02	92·47
7	7·09	11·97	11·06	33	33·43	56·42	52·16	59	59·77	100·87	93·26
7·5	7·60	12·82	11·85	33·5	33·94	57·27	52·95	59·5	60·28	101·73	94·05
8	8·10	13·68	12·64	34	34·44	58·13	53·74	60	60·79	102·58	94·84
8·5	8·61	14·53	13·43	34·5	34·95	58·98	54·53	60·5	61·30	103·44	95·63
9	9·12	15·39	14·22	35	35·46	59·84	55·32	61	61·80	104·30	96·42
9·5	9·63	16·24	15·01	35·5	35·96	60·69	56·11	61·5	62·31	105·15	97·21
10	10·13	17·10	15·81	36	36·47	61·55	56·90	62	62·82	106·01	98·00
10·5	10·64	17·95	16·60	36·5	36·98	62·40	57·69	62·5	63·32	106·86	98·79
11	11·14	18·81	17·39	37	37·48	63·26	58·48	63	63·83	107·72	99·58
11·5	11·65	19·66	18·18	37·5	37·98	64·11	59·27	63·5	64·33	108·57	100·37
12	12·17	20·52	18·97	38	38·50	64·97	60·06	64	64·84	109·43	101·16
12·5	12·68	21·37	19·76	38·5	39·00	65·82	60·85	64·5	65·35	110·28	101·95
13	13·17	22·23	20·55	39	39·51	66·68	61·64	65	65·85	111·14	102·74
13·5	13·68	23·08	21·34	39·5	40·02	67·53	62·43	65·5	66·36	111·99	103·53
14	14·18	23·94	22·13	40	40·52	68·39	63·22	66	66·87	112·85	104·32
14·5	14·69	24·79	22·92	40·5	41·03	69·24	64·01	66·5	67·37	113·70	105·11
15	15·19	25·65	23·71	41	41·54	70·10	64·81	67	67·88	114·56	105·90
15·5	15·70	26·50	24·50	41·5	42·04	70·95	65·60	67·5	68·39	115·41	106·69
16	16·21	27·36	25·29	42	42·55	71·81	66·39	68	68·89	116·27	107·48
16·5	16·73	28·21	26·08	42·5	43·06	72·66	67·18	68·5	69·40	117·12	108·27
17	17·22	29·07	26·87	43	43·57	73·52	67·97	69	69·91	117·98	109·06
17·5	17·73	29·92	27·66	43·5	44·07	74·37	68·76	69·5	70·41	118·83	109·85
18	18·23	30·78	28·45	44	44·58	75·23	69·55	70	70·92	119·69	110·64
18·5	18·74	31·63	29·24	44·5	45·08	76·08	70·34	70·5	71·43	120·53	111·43
19	19·25	32·49	30·02	45	45·59	76·94	71·13	71	71·93	121·39	112·23
19·5	19·76	33·34	30·82	45·5	46·10	77·80	71·92	71·5	72·44	122·24	113·02
20	20·26	34·20	31·61	46	46·60	78·66	72·71	72	72·95	123·10	113·81
20·5	20·77	35·05	32·40	46·5	47·11	79·51	73·50	72·5	73·45	123·95	114·60
21	21·27	35·91	33·19	47	47·62	80·37	74·29	73	73·96	124·81	115·39
21·5	21·78	36·76	33·98	47·5	48·12	81·22	75·08	73·5	74·47	125·66	116·18
22	22·29	37·62	34·77	48	48·63	82·07	75·87	74	74·97	126·52	116·97
22·5	22·80	38·47	35·56	48·5	49·14	82·93	76·66	74·5	75·48	127·37	117·76
23	23·30	39·33	36·35	49	49·64	83·78	77·45	75	75·99	128·23	118·55
23·5	23·81	40·18	37·14	49·5	50·15	84·64	78·24	75·5	76·49	129·08	119·34
24	24·31	41·04	37·93	50	50·66	85·48	79·03	76	77·00	129·94	120·13
24·5	24·82	41·89	38·72	50·5	51·16	86·34	79·82	76·5	77·51	130·79	120·92
25	25·32	42·75	39·51	51	51·67	87·19	80·61	77	78·01	131·65	121·71
25·5	25·83	43·60	40·30	51·5	52·18	88·05	81·40	77·5	78·52	132·50	122·50
26	26·34	44·46	41·09	52	52·68	88·90	82·19				

Böckmann has drawn attention to the importance of always stating the results of the determination of the available alkali of soda ash on the dry material, so as to avoid disputes that may arise from any absorption of moisture that may have taken place during storage. When exposed to the air, soda ash takes up moisture fairly rapidly, and may absorb up to 10 per cent., whilst the loss on ignition of a soda ash properly handled in drawing from the calcining furnace and in packing, is always less than 0·1 per cent. For this reason, it is certainly desirable that the results should be expressed on the dry substance as well as on the sample as received.

General Examination of Soda Ash

Under this heading the following estimations are included, in addition to the alkalinity determination: specific gravity, clearness of the aqueous solution, degree of fineness, matter insoluble in water, oxide of iron, and proportion of sodium chloride and sodium sulphate.

1. Specific gravity or Density (Böckmann).—The term specific gravity, or more correctly density, when applied to soda ash, does not mean the actual specific gravity as determined in the pyknometer, where the intervening space between the various particles of the ash is filled with some liquid, such as benzene, which does not exert a solvent effect. Such a determination is of no practical value, as under these conditions all samples of soda ash, no matter what the method of manufacture, would give approximately equal values, since the impurities, which are only present in small amounts, and do not differ greatly in specific gravity from the soda ash itself (in round figures, Na_2CO_3, 2·5; Na_2SO_4, 2·6; NaCl, 2·1) have but little influence.

It is, however, necessary for many purposes to be able to express in figures the "bulkiness" of the ash, a property depending on the method of manufacture and grinding adopted. The expression refers only to the cubic weight, that is, the weight of soda ash which can be closely packed into a vessel of definite capacity.

Böckmann recommends for this determination a strong cylindrical glass vessel, prepared by cutting off the upper part of a specimen bottle and grinding the edges of the lower part until the capacity is as nearly as possible 100 c.c.[1] It is not essential that the capacity should be 100 c.c., but the employment of a vessel of this size saves a considerable amount of calculation. Any value lying between 99·5 c.c. and 100·5 c.c. may be regarded as representing 100 c.c. for this determination. If, for example, the weight of ash filling such a vessel be 102 g., then the "cubic weight" will be 1·03, 1·02, 1·01 respectively, according as the capacity

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[1] Special bottles for "cubic weight" determination of this capacity are made by Desaga, Heidelberg.

is taken at 99·5, 100·0, or 100·5; that is, a margin of ±0·5 c.c. is allowed. The capacity of the vessel to within 0·1 c.c. and its weight to within 0·1 g. are determined once for all, and both values are etched on the glass. Any similar vessel may of course be used, or even a small strong beaker (without lip) of suitable size, though this is rather apt to get broken.

The ground and dry ash to be examined is filled into the vessel in about six separate portions, the glass being tapped on the table after each addition in order to pack the soda as closely as possible Finally, the ash standing above the top of the vessel is removed by sliding a small glass plate over the rim, after which the vessel and soda are weighed on a balance turning to 0·1 g. The density obtained is calculated to the second decimal place. The results agree to within two units in the second decimal place; it is thus unnecessary to weigh to nearer than 0·1 g.

Concordant results can only be obtained by this method by filling in the ash in small quantities at a time and tapping the glass after each addition, until the particles are thoroughly packed together so that a finger-nail does not make an impression in the mass.

If the ash is filled into the vessel without pressure and tapping, the results are quite different to those obtained by the above method, but they are concordant amongst themselves and are consequently equally applicable in practice. This alternative method is more suited as an empirical test to be used in the packing-room. The vessel may conveniently consist of a box made of well-seasoned wood and having the internal dimensions 40 × 25 × 20 cm., corresponding to a capacity of 20 litres, or similar suitable dimensions to give a capacity of 1 cubic foot. The soda ash is filled in with a clean wooden spade, care being taken to disturb the box as little as possible in introducing the material. The excess of ash is carefully removed by drawing a straight piece of wood over the top of the box, which is then weighed. The weight of the ash × 50 gives the weight of ash per cubic metre.

Another plan for determining the density is to use a metal cylinder about 8·5 cm. high and 3 cm. diameter, filed down so as to hold 62·5 c.c. of water. The weight in grams of ash that fills a vessel of this capacity is also equivalent to pounds per cubic foot, as 1 g. per 62·5 c.c. = 1 lb. per cubic foot.

Soda ash may be divided into three grades, according to the density—"light" (density 0·8 to 1·0), "medium" (about 1·0 to 1·25), and "heavy" (about 1·25 to 1·50).

2. The Clearness of the Aqueous solution (Böckmann).—The examination of the solution for turbidity is made by dissolving 25 g. of the ash in 500 c.c. of warm water in a beaker, and comparing the solution, after cooling, with a standard solution prepared in a similar manner.

The solutions obtained from ammonia-ash are relatively very clear, on account of the great purity of the product; this point is of advantage in colour and similar works. It will, of course, be understood that a commercial product like soda ash always contains traces of impurities and that a perfectly clear solution is not to be expected.

3. **The degree of Fineness** (Böckmann).—The degree of fineness attained in the grinding is only determined in the case of a very heavy ash containing a corresponding proportion of coarser particles, and only then, as a rule, when there is reason to suppose that the grinding has been insufficient. For the determination, 1000-1500 g. of the soda are sieved through a sieve of 35 cm. diameter and 2 mm. mesh, and the coarser particles remaining on the sieve weighed. The amount of the residue should not exceed 5 per cent. of the sample taken.

4. **Insoluble matter** (Böckmann).—Fifty g. of the sample (or 100 g. in the case of a very pure sample) are weighed off in a large beaker on a balance turning to 0·1 g. and sufficient water added to dissolve the ash; the contents of the beaker are agitated gently and continuously to prevent the formation of lumps, which would retard the solution. The whole is then allowed to settle for from $\frac{1}{4}$ to $\frac{1}{2}$ hour in a warm place. As a rule, the insoluble matter settles well, and when this is the case the greater bulk of the solution can be syphoned off or decanted; the remainder is then filtered through a tared filter paper and the insoluble residue well washed with hot water. The two filter papers and insoluble matter are dried at 100° and weighed.

To estimate the iron present in the insoluble matter, the dried and weighed filter is moistened with water and the oxide of iron dissolved in warm hydrochloric acid. The acid filtrate is treated with ammonia, and the precipitated ferric hydroxide filtered off and dissolved in dilute sulphuric acid (1 : 4). The solution is reduced by zinc and then titrated with permanganate. The titration may be made in the hydrochloric acid solution after reducing, diluting largely with water, and adding manganese sulphate solution, but the end-reaction is less sharp in this case.

5. **Sodium chloride.**—Two g. of ammonia-ash, or 5 g. of Leblanc ash, are dissolved in water and nitric acid added until the solution is perfectly neutral or very faintly alkaline to sensitive litmus paper. Potassium chromate is then added and the solution titrated with silver nitrate solution, as described on p. 123; or the determination may be made in acid solution by Volhard's method (p. 123).

6. **Sodium sulphate.**—Five or ten g. of the sample are dissolved in hydrochloric acid and the sulphate precipitated by the addition of a hot solution of barium chloride to the boiling solution.

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The Complete Analysis of Soda Ash

This includes, in addition to the determinations already described, the estimation of the various constituents of the insoluble matter (sand, carbonaceous matter, alumina, calcium carbonate, magnesium carbonate, and ferric oxide), and the estimation of bicarbonate, hydroxide, sulphide, sulphite, silicate, and aluminate of sodium. The five last-named impurities are only found in Leblanc soda. Such gross impurities as sulphide of iron, ferrocyanides, etc., which were formerly met with in Leblanc ash, need hardly be looked for to-day. In addition to the above, it is necessary to determine the moisture, should any opportunity for its absorption have occurred between the times of manufacture and analysis. This may be done by drying in a desiccator over concentrated sulphuric acid, or with greater certainty, by drying for half an hour at 300°, or by gentle ignition (*cf.* pp. 83 and 447).

Before carrying out the various determinations, it is advisable to ascertain whether sodium hydroxide, sodium sulphide, and sodium sulphite are present or not. For this purpose, a portion of the solution is shaken with an excess of barium chloride in absence of air, and the filtrate tested for alkalinity by means of sensitive litmus paper. A second portion of the alkaline solution is tested for sulphide by means of sodium nitroprusside or lead acetate paper, and a third portion examined for sulphite by testing whether the solution after acidifying with acetic acid and adding starch paste will decolorise a dilute solution of iodine.

For the analysis, 100 g. of the ash are weighed into a large beaker, agitated with warm water until solution is complete, the solution allowed to settle for about half an hour in a warm place, filtered through a tared filter paper into a litre flask, the insoluble matter thoroughly washed and the filtrate and washings made up to 1000 c.c.

1. **Sodium chloride.**—Twenty c.c. (= 2 g. ash) in the case of ammonia-ash, or 50 c.c. (= 5 g. ash) in the case of Leblanc ash, are neutralised with dilute nitric acid or dilute sulphuric acid, and titrated with silver nitrate solution (p. 401).

2. **Sodium sulphate.**—Fifty c.c. (= 5 g. ash) in the case of Leblanc soda, or 100 c.c. (= 10 g. ash) in the case of ammonia-soda, are rendered slightly acid by addition of hydrochloric acid and the sulphate precipitated in the hot solution by addition of barium chloride.

3. **Sodium bicarbonate.**—This can only occur in ammonia-soda, and is present only in traces. It is estimated as described on p. 468. At least 5 g. of the sample should be taken and dissolved without agitation in cold water.

4. **Sodium hydroxide.**—This can only occur in incompletely carbon-

ated Leblanc soda or in caustic ash. One hundred c.c. of the solution (= 10 g. ash) are taken and analysed as described on p. 424.

5. **Sodium sulphide.**—This is estimated by Lestelle's method,[1] by titrating 50 c.c. of the solution (= 5 g. ash) with an ammoniacal solution of silver nitrate containing 13·81 g. Ag per litre and corresponding per 1 c.c. to 0·005 g. Na_2S. The solution is heated to boiling, ammonia added, and the silver solution run in drop by drop from a burette, graduated in $\frac{1}{10}$ c.c., until no further precipitation of the dark-coloured silver sulphide results. To get the end-point more accurately it is advisable to filter the solution towards the end of the titration, repeating the filtration as often as may be necessary. Working with the above quantity of solution, each 1 c.c. of silver nitrate solution used corresponds to 0·1 per cent. Na_2S.

The silver solution is prepared by dissolving 13·81 g. pure silver in pure nitric acid, adding 250 c.c. of ammonia solution, and diluting to 1000 c.c.

6. **Sodium sulphite.**—Fifty c.c. of the solution (= 5 g. ash) are acidified with acetic acid, and after the addition of starch solution, titrated with *N*/10 iodine solution till the blue colour appears. Each 1 c.c. *N*/10 iodine solution equals 0·006308 g., or 0·1262 per cent. Na_2SO_3. Or the iodine solution containing 3·249 g. I per litre, described under black ash (p. 425), may be employed, each c.c. of which corresponds to 0·001613 g. or 0.0323 per cent. Na_2SO_3. A deduction must, if necessary, be made for the percentage of sulphide found under test 5, in the ratio of 1·3 c.c. *N*/10 iodine solution, or 5 c.c. of the weaker solution, for each 1 c.c. of the silver solution used.

7. **Sodium silicate and Sodium aluminate.**—One hundred c.c. of the solution (= 10 g. ash) are acidified in a porcelain dish of about 1 litre capacity by the gradual addition of hydrochloric acid. The solution is then evaporated to dryness on the water-bath and finally dried at a higher temperature. On extraction with water, the silica remains behind, and the alumina goes into solution; each constituent is then estimated in the usual way.

The determination of silica and alumina is seldom required, but when it is necessary it is better to weigh off 10 g. of the ash and treat it separately in a porcelain or platinum dish. This prevents any error caused by the alkaline solution attacking the glass vessels used as above. The silicate present in soda ash is too small in amount to interfere with the separation of the carbonate and hydroxide (*cf.* p. 425).

8. **Insoluble matter** (Böckmann).—The filter paper through which the solution of the 100 g. of ash has been filtered is moistened with water and the ferric oxide, alumina, and calcium and magnesium carbonates dissolved by addition of hydrochloric acid. The residue

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[1] *Comptes rend.*, 1862, **55**, 739.

on the filter is well washed with hot water and the filter paper again dried and weighed, against the same paper as tare as before. This gives the sand and carbonaceous matter. The quantity of sand present is estimated by burning the filter paper and insoluble residue in a platinum crucible and deducting from the weight so obtained the ash found on burning the filter paper employed as tare; the difference of the above weighings gives the percentage of sand.

The filtrate containing the portion of the residue soluble in hydrochloric acid is then submitted to the so-called "complete" commercial analysis, which consists in estimating the iron oxide volumetrically as described on p. 380, and taking the rest of the insoluble matter as calcium carbonate; that is, the content in alumina and magnesium carbonate is not taken separately into account, but is looked upon as part of the calcium carbonate. This is sufficiently accurate for technical purposes.

In the method of estimating the available alkali by direct titration of the soda solution, without previous filtration (p. 450), the following substances, if present, are determined in the titration along with the sodium carbonate: calcium and magnesium carbonates, the sesquioxides in the portion insoluble in water, sodium hydroxide, sodium bicarbonate, sodium sulphide, sodium sulphite, sodium silicate, and sodium aluminate. If the titration is made in the filtered solution, any alkalinity due to basic substances in the insoluble matter is excluded. In any case, however, the influence of these impurities, both soluble and insoluble, plays but a small part in the titration of an average ash whether manufactured by the ammonia or Leblanc process, provided the product is not a poor second grade soda. For example, supposing an ash gives on titration a total alkalinity, including that of the insoluble matter, equivalent to 98·4 per cent. Na_2CO_3 and the insoluble matter equals 0·33 per cent., a deduction of 0·3 is made from the total and the percentage of sodium carbonate present put down at 98·1. A 98° soda ash must at least consume acid equivalent to 98 per cent. Na_2CO_3 when the filtered solution is titrated, and the acid used may unhesitatingly be calculated to Na_2CO_3 for commercial purposes, since the soluble impurities are only present in traces and for all the important technical applications of soda ash, with the exception of the manufacture of soda crystals, the impurities will react in the same manner as their equivalent of sodium carbonate.

Should it be necessary, in an exceptional case, to ascertain the real quantity of Na_2CO_3 present as accurately as possible, the sodium carbonate equivalent to the impurities determined as above, is deducted from the total available alkali. The direct estimation of sodium carbonate, that is, of the carbonic acid content, is best made by the gas-volumetric method of Lunge and Marchlewski (p. 149).

A good soda ash should not contain more than 0·4 per cent. of matter insoluble in water, nor more than about 0·1 per cent. insoluble in hydrochloric acid, whilst the ferric oxide should not exceed 0·02 per cent. The impurities present in ammonia-ash frequently fall considerably below these limits.

The amount of sulphate present in ammonia-ash will not exceed 0·1 per cent., unless it has been specially added, whilst in the best Leblanc soda ash it may reach from ½ to 1 per cent., and in ash of low strength may even exceed 8 per cent.

Sodium chloride is present to the extent of from ½ to 2½ per cent. in ammonia-ash according as it is 98° or 96°/98° ash. Good Leblanc ash contains only from ¼ to ½ per cent.

9. Physical and Qualitative Tests.—Various physical and qualitative tests may be advantageously applied to the lower grades of ash made by the Leblanc process.[1]

A good quality of second grade ash should be white in colour even when hot, not yellow or reddish, though it cannot be expected to be as white as "refined alkali." On the other hand, a yellowish product is often found to be better carbonated than a pure white product; this is the case when oxide of iron is present to any considerable extent.

Frequently the ash possesses a bluish tinge, which arises from ultramarine or sodium manganate, either formed in the black ash or, occasionally, purposely added. A grey colour indicates poor carbonating and calcining; such ash will as a rule be found to contain much caustic alkali, together with incompletely oxidised sulphur compounds. Good ash should only show a few dark or red specks after grinding. The proportion of sodium hyroxide should in no case exceed 2 per cent. except in the case of "caustic ash"; if the ash be intended for the manufacture of soda crystals, a maximum of 1 per cent. Na_2O is frequently stipulated, but it is difficult to maintain this exactly, especially when, as in the Tyne works, all the mother liquors are worked up and carbonated, not by gas, but with sawdust. It is, however, readily done when Mactear's mechanical carbonator is employed. The ash should contain at most only very slight traces of sulphide. Even in the case of a moderately calcined and carbonated ash it should be impossible to detect sulphide by means of lead paper, and one drop of iodine should be sufficient to produce a blue coloration when added to a solution containing starch and 1 g. of the soda ash. An alkaline solution containing lead (sodium plumbate) acts better than the ordinary lead paper. Ash manufactured by the Leblanc process always contains minute quantities of sulphur compounds of the lower degrees of oxidation, but these can only be detected when large quantities of the ash, *e.g.*, 50 g. are worked upon. A second quality ash

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 684.

may be regarded as satisfactory in this respect when the oxidisable sulphur compounds present do not exceed 0·1 per cent. of sulphur; for most purposes twice or three times this amount does no harm.

Sodium thiosulphate cannot occur in calcined soda ash, since it would be decomposed in the early stages of calcination. Sodium sulphite, on the other hand, is nearly always present, though in very small amount, in the poorer qualities of ash. Its presence may be detected by iodine solution or other reagents (*cf.* p. 359).

A good second grade ash should not contain more than from 1 to 1¼ per cent. of insoluble matter; 1½ per cent. should be looked upon as a maximum. The insoluble matter consists chiefly of calcium carbonate accompanied by alumina and silica; ferric oxide is only present in traces, except in the case of an ash of reddish-yellow colour and very bad appearance.

The moisture in freshly made ash ranges from ¼ to ½ per cent., and when the ash is well packed it should not rise much over 1 per cent. even after some time. When the moisture reaches 2 per cent. the ash becomes lumpy and discoloured; as already stated, it may absorb up to 10 per cent. of moisture if exposed to a damp atmosphere.

The two neutral salts, sodium chloride and sodium sulphate, which are always present in soda ash, are practically without effect, prejudicial or otherwise, in the quantities normally contained in ordinary ash; this does not, of course, hold when they are purposely added to reduce the strength.

Examination of Chemically pure Sodium Carbonate

According to Krauch,[1] the natrium carb. puriss. generally employed for analytical work contains minute traces of iron, sodium chloride, and sodium sulphate. On this account only the purest and completely anhydrous product, natrium carb. sicc. chem. pur. should be employed for standardising solutions and other similar work. Kissling[2] found Merck's natrium carbonic. sicc. pulv. chem. pur. (for analysis), prepared from natr. carbonic chem. pur. cryst., to consist only of sodium oxide, carbon dioxide, and water; it lost 0·63 per cent. CO_2 and 14·76 per cent. (corresponding to 1 molecule) H_2O at 150°, and therefore contained a little bicarbonate. According to Krauch, ordinary chemically pure anhydrous carbonate contains from 2 to 3 per cent. of water.

The various impurities are tested for as follows.[3]

* *Silica.* From 5 to 10 g. are evaporated with an excess of dilute hydrochloric acid, the residue dried for some time at 100° and

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[1] *The Testing of Chemical Reagents for Purity*, p. 281.

[2] *Chem. Zeit.*, 1890, 14, 136.

[3] The tests marked * are taken from Krauch, *loc. cit.*

then dissolved in a little hydrochloric acid and about 150 c.c. of water; the resulting solution should be clear and free from any flocculent precipitate of silica.

* *Sulphuric acid.* Five g. are dissolved in 75 c.c. of water, the solution made slightly acid by addition of hydrochloric acid, heated to boiling, and barium chloride added; no separation of barium sulphate should be apparent after twelve hours' standing.

* *Sodium chloride.* The slightly acid solution of 2 g. in 20 c.c. of water and dilute nitric acid should remain unaltered on addition of silver nitrate.

* *Arsenic.* Five g. of granulated arsenic-free zinc are placed in a Marsh generating flask of 200 c.c. capacity, dilute sulphuric acid (1 : 3) added and the reagents tested in the usual way for freedom from arsenic. Fifteen g. of the sodium carbonate are then dissolved in a small volume of water, the solution rendered acid by addition of pure dilute sulphuric acid added to the generating flask, and a steady slow evolution of gas maintained for half an hour; no indication of arsenic should occur during this time.

Soluble organic Iron compounds. Twenty-five g. of the carbonate are dissolved in 100 c.c. of lukewarm water, the solution filtered through a pleated filter paper and the filtrate treated with half its volume of sulphuretted hydrogen water. The solution should remain absolutely colourless and show no greenish or dark coloration after standing for an hour. A blank test should be previously made with the distilled water employed.

Krauch (*loc. cit.*) makes a general examination for heavy metals in a similar manner: 20 g. of the carbonate are dissolved in 60 c.c. of water, the solution made acid by hydrochloric acid, and sulphuretted hydrogen water added; no coloration or turbidity should result. The solution should remain equally clear and free from green coloration after addition of ammonia and ammonium sulphide.

* *Phosphoric acid.* Twenty g. of the carbonate are dissolved in 60 c.c. of water, and nitric acid added in considerable excess, followed by a solution of ammonium molybdate. No sign of a precipitate should appear after the solution has been allowed to stand for two hours at a moderate temperature.

Ammonium salts. According to Krauch (*loc. cit.*), several grams of the carbonate are heated in a test tube containing a piece of moistened turmeric paper in the upper part of the tube, which is loosely closed. One-fiftieth of a per cent. of ammonia may be detected in this manner, whilst not less than 1 per cent. of ammonium salts can be recognised by smell without the paper. Detection by smell may be made much sharper by dissolving 10 g. of the carbonate in 500 c.c. of water, and distilling the solution in the apparatus described on p. 311, under Ulsch's method of nitrate estimation, and smelling the gases evolved at the exit-tube from time to time.

* *Sodium thiosulphate.* The aqueous solution is acidified with acetic acid (1 : 50), and tested with silver nitrate. If, at the end of several minutes, the solution only shows a white opalescence (chlorine), it may be taken that neither thiosulphate nor arsenic is present in appreciable quantity. A reddish or yellowish turbidity indicates arsenic, whilst a brown or black turbidity indicates thiosulphate (*cf.* p. 468).

* *Potassium.* The yellow flame coloration produced by the carbonate should not show any, or only a transitory red tinge when viewed through cobalt glass or an indigo prism. According to Krauch, even fractions of a per cent. of potassium salts are sufficient to produce a persistent red coloration in the flame.

* *Sodium hydroxide.* Traces of this impurity are best recognised qualitatively by Dobbin's reagent, ammoniacal potassium mercury iodide. Kissling[1] gives the following method for its preparation. A solution of 5 g. of potassium iodide is treated with a solution of mercuric chloride until the precipitate formed just ceases to redissolve. The solution is filtered, and 1 g. of ammonium chloride added to the filtrate, which is then cautiously treated with sufficient dilute sodium hydroxide solution until a slight permanent precipitate is formed. The solution is finally filtered and the filtrate diluted to 1 litre.

To apply the test, a small quantity of the carbonate solution is placed on a watch-glass and the reagent added; the least trace of hydroxide gives a yellow coloration.

B. Soda Crystals

Ordinary soda crystals consist essentially of decahydrated sodium carbonate, $Na_2CO_3.10H_2O$, which, in the chemically pure state, contains 21·695 per cent. Na_2O, 15·371 per cent. CO_2 (together, therefore, 37·07 per cent. Na_2CO_3), and 62·93 per cent. H_2O. A description of the properties of this salt and of other hydrated compounds of sodium carbonate containing less than 10 molecules of water of crystallisation is given in Lunge's *Sulphuric Acid and Alkali.*[2] The most important of these other salts is known as "Crystal Carbonate," which contains 82·0 per cent. of Na_2CO_3, 17 per cent. of H_2O, and 1 per cent. of other salts (practically $Na_2CO_3.H_2O$), but the quantity made is small when compared with that of the ordinary decahydrated soda crystals.

Commercial soda crystals seldom contain the theoretical quantity of water; either a small excess, which should not exceed 1 per cent., is present, due to the drying only being carried out at ordinary temperature, or there is too little water, owing to weathering, from

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[1] *Chem. Zeit. Rep.*, 1898, **14**, 136.

[2] Vol. ii., pp. 43 and 711.

prolonged exposure to the atmosphere. Weathered soda crystals lose considerably in appearance and this sometimes gives rise to complaint, although the change is entirely in the buyer's favour.

The commercial product is never free from sodium chloride and sodium sulphate. The percentage of sodium chloride should not appreciably exceed 0·5 per cent., whilst the percentage of sodium sulphate, the presence of which is essential for the production of hard crystals,[1] is seldom less than 1 and may rise to 2. A higher percentage of sulphate is to be regarded as inadmissible, especially as it is frequently added as an adulterant. Commercial soda crystals should test at least 34 per cent. Na_2CO_3 by titration, allowing for all impurities; generally 35 per cent. will be found, and in weathered samples the percentage will naturally be still higher. Manufacturers would gladly have a margin extending down to 32 per cent., but this is not always granted.

The estimation of the available alkali and of the impurities is carried out exactly as described under soda ash.

Grosser impurities, such as insoluble matter, iron, etc., were fairly frequent in the yellow crystals common in the early days of manufacture, but they are seldom found in the fine, colourless, transparent crystals which are now supplied. A yellow coloration may be due in part to organic matter.

"Chemically pure crystallised sodium carbonate" (natrium carb. cryst. chem. pur.) is examined as described on p. 460.

C. CAUSTIC SODA

Chemically pure sodium hydroxide can only be obtained by treating metallic sodium with water and is not prepared on the manufacturing scale. Its properties are described in Lunge's *Sulphuric Acid and Alkali*,[2] where Honigmann's table of the boiling points of solutions of sodium hydroxide is also given.

The specific gravity of aqueous solutions of sodium hydroxide has been determined by various observers. Tünnermann's determinations (1827) were made use of by Schiff (1858) for calculating a formula connecting density with concentration and this formula was employed by Gerlach (1867) for the preparation of his table of specific gravities which was in general use until twenty years ago. This table was revised by Hager (1883), and an independent series of determinations were published subsequently by Pickering[3] (1894). Bousfield and Lowry[4] have recently shown that all these determinations are unreliable, owing to the difficulty of preparing solutions of known concentration;

[1] *Cf.* Lunge's *Sulphuric Acid and Alkali*, vol. ii., p. 704.

[2] Vol. ii., p. 81.

[3] *Phil. Mag.*, 1894, **37**, 359; *J. Chem. Soc.*, 1895, **67**, 545.

[4] *Phil. Trans.*, 1905, **204**, 253.

in every case the solutions appear to have been standardised by titration, a method which they have shown to be inaccurate to the extent of from 0·2 to 0·3 per cent. Hager's table is in their opinion less accurate than that of Gerlach; they regard Pickering's relative values for the specific gravity at different concentrations as substantially accurate, but the absolute values as unreliable, to the extent of 0·001 at 50 per cent. sodium hydroxide, and roughly to a proportionate extent at the lower concentrations.

Bousfield and Lowry[1] have accordingly made a fresh series of determinations of the specific gravity of sodium hydroxide solutions, which is given in the following table; the determinations were made at 18° C., but are calculated by means of a series of temperature coefficients to 15° also, in the original paper. The solutions were prepared from weighed quantities of metallic sodium and the densities determined by means of the pyknometer; the values may be regarded as accurate to within 0·01 per cent. of sodium hydroxide, and involve a possible error of 0·0001 in the sp. gr. of a 50 per cent. solution.

Specific Gravity of Solutions of Sodium Hydroxide at 18° C. = 64°.4 F.

NaOH. Per Cent.	Specific Gravity.	NaOH. Per Cent.	Specific Gravity.
0	0·99866	26	1·2860
1	1·01003	27	1·2968
2	1·02127	28	1·3076
3	1·03241	29	1·3184
4	1·04349	30	1·3290
5	1·05454	31	1·3396
6	1·06559	32	1·3502
7	1·07664	33	1·3605
8	1·08769	34	1·3708
9	1·09872	35	1·3811
10	1·10977	36	1·3913
11	1·12082	37	1·4014
12	1·13188	38	1·4115
13	1·14294	39	1·4215
14	1·15400	40	1·4314
15	1·16505	41	1·4411
16	1·17610	42	1·4508
17	1·18714	43	1·4604
18	1·19817	44	1·4699
19	1·20920	45	1·4794
20	1·22022	46	1·4890
21	1·23121	47	1·4985
22	1·24220	48	1·5080
23	1·25317	49	1·5174
24	1·26412	50	1·5268
25	1·27506		

A detailed table, giving the variation of specific gravity with changes of temperature from 0° to 100° at intervals of 10°, is also given by

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[1] *Loc. cit.*

Bousfield and Lowry.[1] A similar table up to temperatures of 50°, but based on the earlier determinations of specific gravity, is given in the *Alkali Makers' Handbook* (p. 143).[2]

It is important to bear in mind that solutions of sodium hydroxide prepared from commercial products show greater variations in the degree of purity than is the case with solutions of sodium carbonate or of acids.

The ordinary rules for sampling, described under "General Methods of Technical Analysis" (p. 7), are not applicable to caustic soda, which comes on to the market in solid blocks packed in iron drums. The block filling the drum is not perfectly uniform throughout; the portions most nearly representing the average are those next to the bottom and sides of the drum, as these portions have solidified fairly rapidly on packing; the central portions which have solidified more slowly are less regular in their composition, as the impurities, more especially chloride and sulphate, have time to accumulate in the fluid core. In sampling, pieces should therefore be taken from as many different parts as possible. In the works the sampling is best done while the material is still liquid; the most satisfactory procedure is to draw three samples from each pot as it is emptied, viz., from the top, the middle, and the bottom respectively, and to pour these, one after the other, on to a plate and to take the middle portion of the whole for analysis. The three lots can subsequently be readily separated, as the surfaces of the layers solidify between the pouring of each sample.

The samples readily take up moisture and carbon dioxide, on the surface, even when preserved in well-stoppered bottles, which is shown by the formation of a bright white crust; this crust should be removed by scraping before the samples are weighed for analysis.

According to Böckmann, the sample should be roughly powdered as rapidly as possible, to prevent absorption of moisture; if single pieces be taken instead of the more homogeneous, coarse powder, differences up to 1 per cent. may result with different portions of the same product. Such powdering is not, however, to be recommended since some absorption of moisture and of carbon dioxide cannot be avoided and may give rise to errors appreciably exceeding 1 per cent.

The chemical analysis of caustic soda is generally confined to the determination of the total alkalinity and of the caustic soda, or more correctly the available soda inclusive of sodium silicate and sodium aluminate. Sodium chloride, sodium sulphate, and water may also be determined. Other impurities are only present in small amount and are consequently only estimated in exceptional cases; the methods described under black ash and soda ash are then employed.

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[1] *Loc. cit.*, p. 279.

[2] *Cf.* also, Wegscheider and Walter, *Monatsh.*, 1905, **26**, 685; 1906, **27**, 13.

Analysis of Caustic Soda.—Fifty g. of the sample, freed from crust by scraping, as described above, are dissolved in water, the solution made up to 1000 c.c., and portions of this solution withdrawn for the following tests.

1. The *Total Alkalinity* is estimated by titrating 50 c.c. of the solution $=2 \cdot 5$ g. substance with normal acid, using methyl orange as indicator. The result is variously calculated according to the scale employed (see p. 451). In England the results are either expressed in percentage of "real Na_2O" or in percentage of "commercial Na_2O," the latter figure being arrived at by multiplying the percentage of real Na_2O by 31·4 and dividing by 31. In Germany the alkalinity is expressed as a percentage of sodium carbonate, and in France in degrees Descroizilles.

2. The *Sodium Hydroxide* actually present may be estimated in various ways. The only other alkaline substance to be taken into account is sodium carbonate; the quantities of aluminate and silicate are extremely minute, except in the case of caustic bottoms (p. 441).

The most exact method of estimating the carbonate is to determine the carbon dioxide evolved on treatment with a strong acid. This may be done either gravimetrically by the Fresenius-Classen method, or more rapidly and accurately by the method of Lunge and Marchlewski (p. 149).

The method depending upon titration with phenolphthalein and hydrochloric acid, after the addition of an excess of barium chloride, (pp. 73 and 424), is almost equally exact. This method gives the caustic soda directly.

For routine testing in the works the method described on p. 73 is to be recommended. It is not quite so accurate as the above, but it has the advantage of rapidity and serves as a check on the total alkalinity (test 1). Fifty c.c. of the solution, preferably cooled nearly to 0°, are titrated first with hydrochloric acid and phenolphthalein until the red coloration just disappears, which occurs when all the sodium hydroxide has been neutralised and the carbonate present has been converted to bicarbonate; methyl orange is then added to the solution and the titration continued until the yellow colour changes to pink. If n c.c. of acid are required for the first part of the titration, and m additional c.c. for the second, $2m$ corresponds to the Na_2CO_3 present and $n-m$ to the NaOH.

3. The determination of *Chloride*, *Sulphate*, and other impurities is carried out as described under Soda Ash, p. 456.

4. *Water*. Caustic soda may contain up to 30 per cent. of water when it reaches a broker or analyst. This is more especially the case when samples have been sent in badly sealed boxes, etc.

In such instances the water cannot be accurately determined by direct heating in a porcelain crucible owing to unavoidable mechanical loss due to small particles being carried away by the escaping steam; on the other hand, if caustic soda be heated in a drying oven to 140° a gain in weight may very easily occur, due to absorption of carbon dioxide; such a gain almost invariably occurs when the water content is low.

The moisture determination is therefore best made as described under Salt (p. 401). About 5 g. of the caustic soda are heated to 150° on the sand-bath for three or four hours in an Erlenmeyer flask of the prescribed dimensions. The funnel must be kept in position the whole time (in this the method differs from that employed in the case of salt), to prevent absorption of carbon dioxide. The flask and funnel are placed on a marble slab, after the heating is completed, allowed to cool in the air, and finally weighed.

Caustic Salts are analysed in the same way as caustic soda.

D. SODIUM BICARBONATE

Sodium bicarbonate, $NaHCO_3$, contains 36·94 per cent. Na_2O, 52·34 per cent CO_2, and 10·72 per cent. H_2O. In the pure condition, that is, when fully saturated with carbon dioxide, it reacts alkaline towards litmus and, according to earlier accepted views, neutral to phenolphthalein. Küster[1] states that in dilute solution it reddens phenolphthalein in consequence of hydrolysis and Siemens[2] has found that such reddening is produced by even the purest bicarbonate. The solubility and other properties are described in Lunge's *Sulphuric Acid and Alkali*.[3]

On exposure to the air the powder loses carbon dioxide, even at the ordinary temperature, and much more rapidly at somewhat higher temperatures. The aqueous solution, in a similar manner rapidly, parts with some of its carbon dioxide and is then found to contain appreciable quantities of the normal carbonate.

Commercial bicarbonate is very seldom absolutely free from normal carbonate, but the quantity of the latter should only be very small. Bicarbonate should dissolve in water to a perfectly clear solution and chloride and sulphate should only be present in traces. Formerly bicarbonate was frequently found to contain sodium thiosulphate, due to its having been manufactured from Leblanc soda liquors by the Deacon-Hurter process. Bicarbonate manufactured by the ammonia-soda process may contain a little ammonia as carbonate or chloride, but at the present time the high percentage (2·6 per cent. ammonium carbonate) found by Lehmann[4] is not likely to occur; a much smaller percentage than this would make itself evident by the odour.

Bicarbonate of soda is very largely used in medicine and in bakeries,

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[1] *Z. anorg. Chem.*, 1896, **13**, 127.

[2] *Fischer's Jahresber.*, 1897, 455.

[3] Vol. ii., p. 54.

[4] *Chem. Ind.*, 1887, **10**, 88.

and it should consequently not contain metallic impurities in sufficient quantity to be detectable by sulphuretted hydrogen or by ammonium sulphide. The detection of small quantities of arsenic is carried out as described in p. 362.

Qualitative analysis of Sodium bicarbonate—This is directed in the first place to the examination for chloride and sulphate, which impurities should only be present in very small quantity; this applies also to ammonia. Thiosulphate is detected, according to Mylius,[1] by adding dilute sulphuric acid and zinc, and examining for sulphuretted hydrogen by means of lead paper. The methods of Salzer[2] and of Lüttge[3] are less exact. Salzer adds a drop of iodine solution to the cold saturated solution of the bicarbonate; if thiosulphate is present, the iodine is decolorised. Lüttge treats the bicarbonate with excess of hydrochloric acid and then adds barium nitrate. According to Musset,[4] very small amounts of thiosulphate can be detected by the grey coloration due to mercuric sulphide, which is formed when 5 g. of the bicarbonate are ground with 0·1 g. of calomel and two drops of water.

Thiocyanates are detected, according to Utescher,[5] by agitating a large quantity of the bicarbonate with water and testing the solution obtained with ferric chloride in hydrochloric acid solution.

Several methods for detecting the presence of the normal carbonate in bicarbonate are known. The methods depending upon the reddening of phenolphthalein are, according to Küster's observations, (*cf.* p. 467) inaccurate. The method usually employed is the reaction with mercuric chloride. A solution of mercuric chloride in two parts of water is added to a solution of the bicarbonate in fifteen parts of water, when a white cloudiness, which gradually becomes brown after several minutes, is produced. This method is, however, by no means reliable, and the same may be said of all other qualitative tests for the normal carbonate. The presence of the normal carbonate can only be proved with certainty by a quantitative examination.

The detection of normal carbonate by means of magnesium sulphate is absolutely untrustworthy. It is better, according to Leys,[6] to employ a saturated solution of calcium sulphate which, in the presence of sodium carbonate, gives a precipitate of amorphous calcium carbonate, which is easily distinguishable from the crystalline calcium sulphate.

Kubli[7] recommends the use of quinine hydrochloride, which is not precipitated by bicarbonate containing less than 2 per cent. of normal carbonate.

Quantitative analysis of Sodium bicarbonate consists in de-

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[1] *Fischer's Jahresber.*, 1886, 282.

[2] *Chem. Ind.*, 1887, **10**, 27.

[3] *Chem. Zeit. Rep.*, 1889, **13**, 305.

[4] *Z. angew. Chem.*, 1890, **3**, 311.

[5] *Apoth.-Zeit.*, 1888, 610.

[6] *Chem. Centr.*, 1898, **I.**, 752.

[7] *Ibid.*, 1898, **II.**, 416.

termining the percentage of available alkali and of carbon dioxide. As a matter of fact, the latter determination alone is sufficient.

The indirect method of estimating total carbon dioxide by driving it off and noting the loss of weight in one of the known form of apparatus, is certainly not sufficiently exact. Trustworthy results can only be obtained by estimating the carbon dioxide directly, either gravimetrically by absorption with soda lime, etc., or gas-volumetrically by the method of Lunge and Marchlewski as modified by Lunge and Rittener (p. 153).

The method described on p. 429 may also be employed, but since this necessitates bringing the bicarbonate into solution, care must be taken to avoid loss of carbon dioxide during this operation. The estimation is carried out as follows:—

5·0 g. are weighed off in a small beaker and dissolved in about 100 c.c. of water which has been previously thoroughly boiled and again cooled to 15° to 20°. Solution is effected in a large beaker of 900 to 1000 c.c. capacity, agitation of the solution being avoided as far as possible; the operation may be assisted by cautiously breaking up any lumps of bicarbonate that remain on the bottom of the beaker with a glass rod, care being taken not to stir up the solution at all violently. Unless these precautions be observed, loss of carbon dioxide may easily occur and the results obtained will not be reliable. The water employed should not be below 15° nor above 20° in temperature; in the former case, solution is difficult, and in the latter, loss of carbon dioxide is likely to result.

Ten g. of pure sodium chloride are then added to the solution, which is cooled to nearly 0°, and titrated with $N/1$ hydrochloric acid, using phenolphthalein as indicator, the titration being carried to the point where the red colour just vanishes ($=a$ c.c. acid). The delivery end of the burette should dip into the solution. Methyl orange is next added, and the titration continued until the colour changes to yellow ($=b$ c.c. acid). $2a$ c.c. correspond to the alkali present as Na_2CO_3, and $b-a$ to that present as $NaHCO_3$ (*cf.* p. 429).

Sundström's method,[1] which consists in adding sodium hydroxide to the bicarbonate solution until the latter has been converted into carbonate, this point being determined by the brown coloration produced by spotting with silver nitrate, has been examined by Lunge[2] and found to be reliable. It is, however, less convenient than the method described above, and is in no way more accurate.

Estimation of the total Carbon dioxide. This is a more reliable check than the above on the composition of bicarbonate; the quantity should at least reach 50 per cent. (Theory, 52·34 per cent.). The best plan is to determine the carbon dioxide present as bicarbonate

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[1] Private communication to Prof. Lunge.

[2] *Z. angew. Chem.*, 1897, **10**, 169.

directly. A simple, rapid and exact method for this determination has been described by Lunge,[1] which consists in heating the sample to a certain definite temperature and estimating the carbon dioxide driven off; the method is only applicable to solid bicarbonate and not to solutions.

The apparatus shown in Fig. 138 is employed in carrying out the test. It is connected with a bulb-nitrometer (p. 136), or preferably, with a gas-volumeter (p. 138), or with any other suitable apparatus for measuring or weighing the carbon dioxide evolved.

A glass tube, 65 mm. long and 6 mm. internal diameter, is connected at one end with a wider tube, provided with a tightly fitting ground-in stopper, *a*, and at the other end with a capillary tube, *d*, 60 mm. long. The stopper *a* is continued in the form of a glass rod, *b*, 30 mm. long, which, whilst not ground into the tube, fits it fairly tightly. This leaves a free space, *c*, 35 mm. long and 6 mm. diameter, which is separated from the capillary by means of a small plug of asbestos or glass-wool. This free space will hold about 0·850 g. of powdered bicarbonate, a quantity which, provided the quality be good, will give rather more than 110 c.c. of carbon dioxide, measured at 0° and 760 mm. This volume can be readily measured in the universal gas-volumeter, which is graduated from 1 to 30 c.c. and from 100 to 140 c.c., the intervening space being taken up by the bulb. Should the free space in the decomposition tube be too small or too large for the measuring apparatus employed, it may be altered by making the glass rod *b* shorter or longer, as may be necessary.

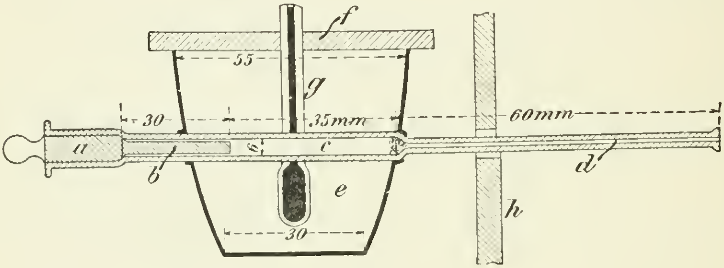

FIG. 138.

The stopper extension *b* allows the space *c* to be well heated without risk of cracking the ground-in portion *a*, and so permits this part to be made perfectly tight by using a little vaseline or other grease.

The heating is effected in the air-bath *e*, which consists of an iron crucible bored in two corresponding positions on opposite sides and covered with a piece of asbestos card, *f*, through which the thermometer *g* is placed. A sheet of asbestos card, *h*, is fixed over the capillary *d*;

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[1] *Z. angew. Chem.*, 1897, **10**, 522.

this card extends below the flame used to heat the crucible *c* and thus protects the gas-volumeter from the heat; an interval of at least ten minutes must be allowed after each operation before the volume of gas collected is adjusted and read off.

To carry out the determination, the tube is first weighed empty, then filled with bicarbonate and again weighed. Care must be taken that none of the bicarbonate remains in the portion fitted with the stopper *ab*; any particles adhering to the walls in this portion of the tube must be removed by a rubber-covered rod or other suitable contrivance before the stopper, which should be covered with a little vaseline, is inserted. The tube is then placed in the air-bath, as shown in Fig. 138, so that the whole of the bicarbonate gets heated, and the free end of the capillary *d* connected with the side capillary tube of the gas-volumeter. The small capillary space between these two tubes is evacuated two or three times by lowering the levelling tube of the volumeter until a vacuum exists in the measuring tube, shutting off from the capillary and expelling the air from the measuring tube by raising the levelling tube. Three such evacuations may be carried out in the space of a minute. The levelling tube is then lowered and the air-bath heated by a flame of moderate size to between 260° and 270°, an operation requiring on the average about seven minutes. The heating is continued for a further three minutes, after which the tap connecting the capillary with the measuring tube is closed, the apparatus allowed to stand for about ten minutes to attain the atmospheric temperature and the levelling and reduction tubes adjusted in the usual manner to allow the volume of gas evolved to be read off directly as dry gas corrected to 0° and 760 mm. Since the gas is always collected moist in this determination the reduction tube must be set accordingly; the condensation of water is very small and exerts no influence on the reading. The percentage of carbon dioxide may be calculated directly from the volume read off, since the free capillary space is so small that no appreciable quantity of air remains after evacuating three times as described above. Lunge, however, recommends transferring the gas, after measurement, to an Orsat apparatus and proving that it is completely absorbable by alkali hydroxide, which he finds is always the case. One c.c. dry CO_2 at 0° and 760 mm. pressure weighs 1·9766 mg., and corresponds to 7·5524 mg. $NaHCO_3$. To arrive at the actual percentage of bicarbonate in the sample examined, the figure 7·5524 is multiplied by the number of c.c. of gas liberated and divided by the weight of substance taken. If it be desired to also determine the amount of normal carbonate present, a second portion of the sample may be titrated with normal acid and methyl orange, or the total carbon dioxide liberated by decomposing with hydrochloric acid may be determined (p. 149). In the latter case, twice the volume of carbon dioxide found in the bicarbonate estimation is deducted from the total carbon dioxide found, and the remainder calculated to normal carbonate.

The residue in the decomposition tube used in the determination of the bicarbonate can be washed out and titrated; this saves a weighing, but it is scarcely as accurate as the titration of a separate portion, owing to the risk of losing some of the material. This estimation of normal carbonate is, as a rule, unnecessary.

THE EXAMINATION OF COMMERCIAL LIQUID CARBON DIOXIDE

The following particulars are taken from a very complete investigation of the subject by Lange.[1] In determining the value of commercial liquefied carbonic acid it is, as a rule, sufficient to find out what proportion of gases not absorbable by potassium hydroxide solution is contained in the liquid. It is generally unnecessary to determine the volume of air present in the gas space of the cylinder. This and the determination of the carbon dioxide present in the gas space need only be done in very exact work, when a series of samples otherwise similar have to be examined. In determining the percentage of air in samples of the gas drawn from the cylinder, it will generally suffice to estimate the carbon dioxide in the gas space before and after the taking of the sample. The percentage of air present in the sample is then taken as the mean of the two determinations, provided that the carbon dioxide last examined is not perfectly air-free.

Any suitable form of apparatus for gas analysis may be employed for the determination of the contained air. Lange makes use of the modified Winkler gas-burette shown in Fig. 139.

The tube A has a capacity of 100 c.c. and is narrowed at the top to a tube of 5 c.c. capacity, graduated in $\frac{1}{20}$ c.c. It is connected at its lower end with the tube B by means of a piece of rubber tubing; a run-off tap is not provided. The bent tube *e* is connected by a length of rubber tubing with a glass tube, which dips into about 250 c.c. of the solution contained in the bottle D, clamped to the stand. To charge the apparatus, potassium hydroxide solution of sp. gr. 1·297 is introduced into B in sufficient quantity to more than half fill the tubes B and A; the stopper carrying the bent tube *e* and the attached rubber tubing is then fixed in position in B, and the alkali solution driven out of the tube A by blowing through a rubber tube attached above the tap *b*. The tap *a* is closed as soon as the level of the liquid in A has sunk below the tap. The tube B is then filled up with potassium hydroxide solution and fixed at such a height on the stand that on opening the tap *a* the solution exactly fills the bore of the latter.

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[1] *Chem. Ind.*, 1900, 23, 530.

The apparatus is then ready for use. The tap *a* is turned through 90° and the gas to be examined introduced; on closing the tap *b* and opening *a*, the absorbent solution flows from D into B and A. After the absorption is completed the tap *b* is opened, when the solution flows back again into D until the level of the liquid reaches the tap *a*, where it remains, leaving the apparatus ready for a further test. More than 400 analyses can be made with a single charge of solution.

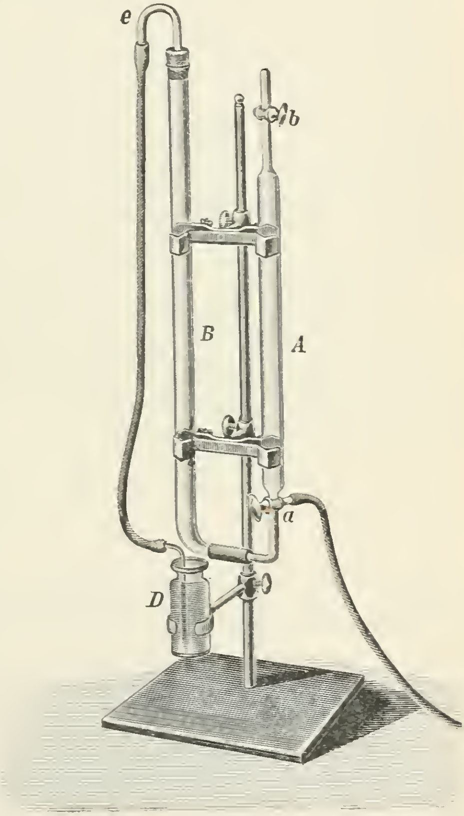

Fig. 139.

The examination of the carbon dioxide is carried out as follows. An adapting piece is screwed, using some luting material, into the outlet pipe of the cylinder, which is placed in a vertical position, and a piece of rubber tubing attached to the adapter. The cylinder valve is then opened and carefully regulated, so as to give a steady and not too rapid current of the gas when the rubber tube is connected with the tap *a*, which is so turned that the gas enters the tube A, driving out the contained air through the tap *b*. After a minute the tube A will be filled with the gas; the operation may, however, be continued until needle-shaped crystals of potassium bicarbonate are formed in the upper narrow portion of A. The tap *b* is then closed, and after the gas in A has been brought to atmospheric pressure by removing the rubber tubing, the tap *a* is turned through 90° to bring A and B into communication. The potassium hydroxide solution immediately rises in A; the absorption may be hastened by gradually turning A into a nearly horizontal position. Towards the end of the absorption the tube is tilted to and fro and then clamped. The bottle D is then raised until the levels of the liquid in A and D are the same, and the volume of the gas read. When many determinations have to be made, the adjustment with D may be dispensed with and the volume read directly by the aid of a suitable correction table. The difference between two successive tests should not exceed 0·05 per cent. by volume. By graduating the upper part of the tube in $\frac{1}{20}$ c.c., it is possible to approximate to $\frac{1}{100}$ c.c. in the readings, and so obtain very accurate results.

To draw a sample from the liquid contents of the cylinder, it should be laid on its side, on a suitable support, so that the outlet tube of the valve points upwards. As a rule, it will be found possible to obtain a satisfactory and not too violent current of gas by slowly and cautiously opening the valve; small particles of solid carbonic acid will always be found to issue with the gas. In some cases the setting of the valve is very troublesome and the current of gas is so violent and intermittent that a very slight turning of the valve may cause the rubber tubing to burst. When this is the case a reducing valve may be inserted and the gas allowed to issue for some considerable time to thoroughly replace the air in the reducing valve before the sample is taken.

The calculation is carried out as follows:—

If 1 kilo of carbon dioxide corresponds, at the temperature at which the analysis is carried out, to A litres, then the calculated G_1 kilos with k_1 volume per cent. CO_2 occupy a volume of $G_1 . A . 0{\cdot}01 k_1$; in all, G kilos or GA litres are present. The volume per cent. of CO_2 present in all, is thus given by the equation:—

$$GA : 100 = (G_1 . A . 0.01 k_1 + G_2 . A . 0.01 k_2) : x$$

$$\text{or} \quad x = \frac{G_1 k_1 + G_2 k_2}{G}$$

or, more conveniently for calculation, the total quantity of air present in the carbonic acid is given by the equation:—

$$y = \frac{G_1(100 - k_1) + G_2\,(100 - k_2)}{G}$$

That is, the carbon dioxide present in the cylinder in the liquid and gaseous states respectively is first calculated to weight; each weight is then multiplied by the corresponding percentage of air in the liquid and gaseous portions and the products added together. The true average air content of the total carbon dioxide, in volume percentage, is then found by dividing the figure obtained above by the net weight of the contents of the cylinder.

The methods for the examination of liquid carbon dioxide have been more recently investigated by Thiele and Deckert,[1] who have pointed out the importance of determining the gases other than carbon dioxide, and the difficulty of doing so if the carbon dioxide is de-

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[1] *Z. angew. Chem.* 1907, **20**, 737.

termined by a gas-volumetric process, owing to the small volume of the residue. They accordingly recommend a method in which the carbon dioxide is absorbed over potassium hydroxide in a special measuring tube, fitted into a flask, which is weighed before and after the absorption. A considerable volume of the unabsorbed gases is thus obtained, which is transferred to a gas-volumeter for measurement and subsequently analysed if desired; the increase in weight of the flask gives the content of carbon dioxide.

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THE CHLORINE INDUSTRY

By Professor G. LUNGE; translated by JAMES T. CONROY, B.Sc., Ph.D.

RAW MATERIALS

THE raw materials employed in the Weldon process and for the preparation of chlorine on a small scale, are hydrochloric acid, the examination of which has already been described (p. 409), and native manganese peroxide; the latter is necessary in the Weldon process to make good the loss of manganese that occurs in the operations involved. In the Deacon process hydrochloric acid is the only raw material; in the various electrolytic processes the raw material is either potassium chloride or sodium chloride.

In the Weldon process for regenerating the manganese dioxide, lime, or milk of lime, is required. The lime employed is very frequently prepared by burning limestone in the works where it is used. Certain special properties are essential in lime intended for this purpose. Slaked lime is also required in the manufacture of bleaching powder and milk of lime in the manufacture of potassium chlorate. The method of examining the potassium chloride employed in the latter industry is given in the section on "Potassium Salts" (p. 533). This section is restricted to the methods employed for the examination of manganese ore, quick lime, slaked lime and milk of lime.

I. MANGANESE ORE

Native manganese ore consists of manganese dioxide admixed with larger or smaller quantities of impurities. A description of the various minerals in which it is present, the localities in which they occur, etc., will be found in Lunge's *Sulphuric Acid and Alkali*.[1]

The technical examination of manganese ore intended for use in Weldon stills, is confined to the estimation of moisture, active oxygen, carbon dioxide, and to the quantity of hydrochloric acid necessary for decomposition.

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[1] Vol. iii., p. 268.

1. **Moisture.**—According to R. Fresenius, manganese ore only parts with the whole of its hygroscopic moisture at 120°; at higher temperatures a portion of the combined water is also driven off. The method of drying recommended by Fresenius based on this consideration, is, however, not followed in works, the practice being to dry the ore at 100° in the following manner.

A fair quantity of the very finely ground ore is weighed off, and spread out in a thin layer on a large watch-glass, and heated directly on a briskly boiling water-bath, or at 100° in a drying-oven, until the weight is constant. Drying should be complete after four hours; if it be continued for six hours, it is safe to assume that constant weight has been attained.

2. **Active Oxygen** is always expressed as percentage by weight of manganese dioxide. This includes all oxygen combined to form oxides higher than manganous oxide, MnO; or in other words, all oxygen capable of reacting with hydrochloric acid to liberate chlorine. One part active oxygen $= 5{\cdot}438$ parts MnO_2.

Of the many methods of estimation which have been proposed, only a few are actually employed. Gay-Lussac's method, which consisted in measuring the volume of oxygen liberated on boiling the ore with concentrated sulphuric acid, has gone completely out of use. A method formerly much used is that of Berthier and Thompson, as modified by Fresenius and Will; it depends on the oxidation of oxalic acid according to the equation:—

$$MnO_2 + H_2SO_4 + C_2H_2O_4 = MnSO_4 + 2H_2O + 2CO_2.$$

The ore is warmed with strong sulphuric acid and oxalic acid, and the carbon dioxide liberated thoroughly dried before leaving the apparatus; the weight of real MnO_2 (or its equivalent) in the sample is then calculated from the loss in weight arising from the liberated carbon dioxide. Any carbon dioxide due to the presence of carbonate in the ore must, of course, be allowed for. The method is subject to the error, common to all determinations in which a small loss of weight is obtained as the difference between two weighings of a relatively heavy piece of apparatus, and which is now known to be much greater than was previously supposed. In addition there are other sources of error, especially those arising from the difficulty in dissolving many of the ores. The proposal to weigh the carbon dioxide directly by absorbing it with soda lime only partially overcomes these objections.

Better results are obtained by applying the reaction volumetrically, by starting, for example, with a known weight of oxalic acid and titrating back the excess with permanganate solution; this modification[1] has not, however, found any extended application in works practice.

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 274.

The same may be said of Bunsen's method, which consists in boiling the ore with strong hydrochloric acid, absorbing the evolved chlorine in potassium iodide solution, and titrating the liberated iodine with sodium thiosulphate. In principle this method ought to be the best, since it most nearly corresponds to the technical application of the ore. Correct results can, however, only be obtained by the very careful observation of various precautions and by carrying out blank tests. Consequently, the method is but seldom employed, notwithstanding the fact that the labour involved has been greatly reduced by the introduction of convenient apparatus.[1]

The method most generally adopted is the "Ferrous Sulphate" method of Levol and Poggiale. Carried out in the following manner described by Lunge, the process is looked upon as a standard method in the heavy chemical trade, as it is convenient and exact, and gives concordant results in the hands of different analysts.

1·0875 g. of the very finely ground ore thoroughly dried at 100° are treated in a round-bottomed flask fitted with a Bunsen valve, or still better with a Contat bulb (Fig. 39, p. 106), with 75 c.c. of acid ferrous sulphate solution which is added from a pipette in three portions of 25 c.c. at a time. The ferrous sulphate solution is prepared by dissolving 100 g. of pure ferrous sulphate and 100 c.c. of pure concentrated sulphuric acid in 1 litre of water; it should be standardised daily when in use with $N/2$ permanganate solution, using the 25 c.c. pipette employed in the tests (*cf.* p. 103). After the addition of the ferrous sulphate solution, the flask is heated until the whole of the manganese dioxide has gone into solution and the insoluble residue is no longer dark coloured. The Bunsen valve must, of course, remain gas-tight during the subsequent cooling. Occasionally the external pressure is sufficient to break the flask when a Bunsen valve is employed; for this reason the Contat bulb is to be preferred, since it allows a solution of sodium bicarbonate to enter the flask during the cooling, and the carbon dioxide liberated effectually keeps out atmospheric oxygen whilst maintaining the normal pressure. When the flask and contents are quite cold the solution is diluted with from 100 to 200 c.c. of water, and titrated with permanganate until the faint rose-tint ceases to disappear instantaneously on stirring the solution, and remains permanent for at least half a minute; subsequent decoloration may be disregarded. The quantity of permanganate solution required is deducted from that corresponding to the 75 c.c. of ferrous sulphate solution; each 1 c.c. of the remainder corresponds to 0·02175 g. MnO_2, or for the weight of ore taken above, to 2 per cent. MnO_2.

Another method, characterised by extreme rapidity, and which is

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 274.

very useful as a check on the above, is Lunge's[1] gas-volumetric method, based on the interaction of peroxide of hydrogen and manganese dioxide according to the equation :—

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2.$$

The value of the peroxide is determined by the volume of oxygen evolved, which, as will be seen from the above equation, is equal to twice the quantity of "active oxygen" present in the manganese dioxide, the hydrogen peroxide being of course present in excess. Each 1 c.c. of oxygen evolved at 0° and 760 mm. corresponds to 0·003885 g. MnO_2. If 0·1943 g. of the manganese ore be taken for analysis, each 1 c.c. of oxygen evolved = 2 per cent. MnO_2; and if 0·3885 g. ore be taken, each 1 c.c. of oxygen = 1 per cent. MnO_2. The former quantity is suitable for small nitrometers, the latter for the larger apparatus.

The operation is carried out in the nitrometer with the auxiliary flask as described on p. 137, the volume of gas obtained being reduced to the volume of dry gas at 0° and 760 mm. It is, however, more convenient to employ the "Gas-volumeter" (p. 138), whereby the corrected volume is obtained without calculation.

The following points should be observed when carrying out this test. The ore must be ground until extremely fine, so as to allow of complete decomposition and the quantity weighed off must be placed in the outer compartment of the decomposition flask, care being taken that none gets into the inner compartment; a few c.c. of dilute sulphuric acid are first added to decompose any carbonate present in the sample. Hydrogen peroxide is then placed in the inner compartment, an excess over the amount necessary to decompose the ore being added and the bottle tightly closed by the rubber stopper connected with the nitrometer tap. The pressure is equalised by opening the tap to the air, so that the mercury comes to the zero point of the nitrometer. In placing the stopper in the decomposition flask, and also in the subsequent shaking, the flask should be held by the neck only, so as to avoid warming by the hand as far as possible: a more satisfactory plan is to allow the bottle to stand for at least ten minutes in water, at the room temperature, both before and after the decomposition. After the mercury has been brought to the zero mark the flask is tilted, so that the hydrogen peroxide flows from the inner compartment on to the ore, and the bottle is then shaken. Shaking should only be continued for two minutes, since after this period there is a risk of the insoluble matter acting upon the hydrogen peroxide with spontaneous evolution of oxygen. Shaking for a longer period is to be avoided, even in cases where decomposition is incomplete owing to insufficient grinding. In-

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[1] *Ber.*, 1885, **18**, 1872; *Z. angew. Chem.*, 1890, **3**, 8 and 75; *cf.* also, Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 278.

complete decomposition is evidenced by the presence of dark material in the otherwise light coloured residue of silicate; longer agitation does not aid the decomposition, but only promotes the spontaneous decomposition of the peroxide. The level of the mercury should be adjusted and the volume of gas read as soon as the initial temperature has been attained.

The evolved gas may be regarded as fully saturated with aqueous vapour, and the reduction should be made by the aid of the "moist reduction tube" (p. 140); should the apparatus be provided with a "dry reduction tube," the correction must be carried out as described on p. 141.

A. Baumann[1] employs an azotometer for the decomposition (p. 125), and to avoid calculating the gas volume to 0° and 760 mm., weighs off a quantity of ore corresponding to the temperature and barometric pressure; this is facilitated by means of a table giving the quantity to be weighed off under varying conditions. The use of such a table does not allow of any variation in temperature between the time of weighing off the ore and the time of making the analysis, and since a difference of 1° C. means a rise or fall of 0·4 per cent. in the result, this point is of considerable importance.[2]

A. Baumann[3] has also devised a volumetric method based on the same reaction. The manganese ore is allowed to react with an excess of hydrogen peroxide, previously standardised by permanganate solution, and the excess of peroxide is titrated back. The hydrogen peroxide solution employed is prepared by diluting the commercial peroxide with dilute sulphuric acid (1 : 10) until the mixture will decompose approximately its own volume of permanganate solution. For the analysis 0·4 to 1·0 g. of the very finely ground manganese ore is weighed off, and treated in a tall beaker or in a flask with exactly 50 c.c. of the hydrogen peroxide solution The mixture is shaken at frequent intervals during half an hour, after which time any undecomposed hydrogen peroxide is titrated with permanganate solution. Should there be between five to ten samples for analysis, the first will be ready for titration when the measured volume of peroxide solution has been added to the last sample, and the various lots can be titrated in the order in which they were weighed off. In some cases exact titration is rendered difficult owing to the ore forming a markedly turbid brown coloured solution. This difficulty may be overcome by carrying out the decomposition in a 100 c.c. graduated flask, making the solution up to 100 c.c. after half an hour, when decomposition is complete, filtering through a double filter paper, and taking 50 c.c. of the filtrate for titration. The number of c.c. required must be doubled for calculating the results on the quantity weighed off.

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[1] *Z. angew. Chem.*, 1890, 3, 78.

[2] *Cf.* Lunge, *ibid.*, 136.

[3] *Ibid.*, 72.

MacLachlan[1] is of opinion that the estimation of the active oxygen in hydrogen peroxide by means of an acid solution of potassium permanganate is altogether unreliable. Lunge maintains that this view only applies to the volumetric determination, and accordingly Baumann's method is to be regarded as inexact until further investigation proves the contrary. Lunge has fully confirmed the accuracy of the gas-volumetric method by a large number of tests.

3. **Carbon dioxide.** — This estimation is important, since carbon dioxide constitutes a very harmful impurity in chlorine intended for the manufacture of bleaching powder. Traces of carbonate may be detected by stirring the powdered ore on a watch-glass with water until all adhering air-bubbles have been removed, then adding a little dilute hydrochloric acid, and viewing the surface of the solution from the side. The liberated carbon dioxide comes off in the form of small, briskly evolved gas-bubbles, and cannot possibly be confused with air. The quantitative determination may either be carried out gravimetrically by liberating the carbon dioxide with dilute sulphuric or nitric acid, and absorbing in soda lime, or still better and more rapidly, by the gas-volumetric method described on p. 149. A good ore should not contain more than 1 per cent. of carbon dioxide.

4. **The Hydrochloric acid necessary for decomposition.**—One g. of the ore is dissolved in 10 c.c. of strong works acid of known strength, the operation being carried out in a flask provided with a reflux condenser, and solution assisted by heating. The solution is then allowed to cool and normal sodium hydroxide added until the separated reddish-brown, flocculent precipitate of ferric hydroxide no longer dissolves on shaking. The volume of sodium hydroxide solution required is calculated to the strength of the acid employed for the decomposition, and the figure thus obtained for the excess of acid deducted from 10, the number of the c.c. of acid taken in the first instance.

Débourdeaux[2] recommends determining the chlorine value and the requisite acid in a single operation. The ore is treated with a mixture of oxalic and sulphuric acids, and after solution the excess of the former is determined by titration with permanganate, and the acid used by titrating with ammonia and fluorescein. This method is not likely to effect any saving of time.

II. LIMESTONE

A description of the characteristics of the most suitable limestone for the manufacture of bleaching powder is given in Lunge's *Sulphuric Acid and Alkali*.[3] The properties required in lime intended for the

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[1] *Chem. Soc. Proc.*, 1903, **19**, 216.

[2] *Comptes rend.*, 1904, **138**, 88.

[3] Vol. iii., p. 440.

Weldon process are somewhat similar; much depends in both cases on the absence of magnesia. The technical examination is carried out as follows:—

1. **Insoluble matter.** — One g. of the limestone is treated with hydrochloric acid, and the insoluble residue thoroughly washed, dried, and ignited. Should appreciable quantities of organic matter be present, the insoluble matter is first weighed on a tared filter paper, after drying at 100°, and then ignited; the difference between the two weighings gives the organic matter.

2. **Lime.**—One g. of the limestone is dissolved in 25 c.c. of normal hydrochloric acid and the excess of acid determined by titration with normal sodium hydroxide solution. The number of c.c. required is deducted from 25; the remainder multiplied by 2·806 gives the percentage content of CaO, or multiplied by 5·006, the percentage content of $CaCO_3$. This method of calculating the result gives any MgO present in terms of CaO but this is quite permissible in limestones intended for use in alkali and bleaching powder works, since they should contain only very little magnesium oxide.

For the same reason, it is equally permissible to calculate the lime content from a determination of the carbon dioxide.

The latter is very frequently determined by loss. Very many forms of apparatus for this purpose are in use.[1] The most rapid and accurate method is the gas-volumetric method described on p. 149. If 0·4497 g. of the sample be taken, each 1 c.c. of gas obtained, measured at 0° and 760 mm., corresponds to 1 per cent. $CaCO_3$.

Should the limestone contain appreciable quantities of sesquioxides, these must first be removed by precipitation with ammonia (free from carbonate), and the calcium then precipitated as oxalate. In exact work the precipitates should be dissolved and reprecipitated (*cf.* p 405). According to Passon,[2] this separation may be obviated by adding phenolphthalein to the acid solution of the limestone, and then sufficient ammonia to produce a distinct red coloration after precipitation is complete. A 10 per cent. solution of citric acid is then added until the colour disappears and the precipitate goes into solution, after which a further 10 c.c. of citric acid solution is added, the whole diluted with water, and the calcium precipitated by the addition of ammonium oxalate to the boiling solution. Iron, aluminium, magnesium, and phosphoric acid do not interfere when this method of precipitation is adopted.

3. **Magnesia** is, as a rule, only determined in limestone intended for use in the manganese recovery process, or in the manufacture of bleaching powder. Two g. of the sample are dissolved in hydrochloric

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[1] *Cf.* Clowes and Coleman, *Quantitative Analysis*, 6th edition, 1903, p. 128; Treadwell, *Analytical Chemistry*, vol. ii., p. 292.

[2] *Z. angew. Chem.*, 1898, **11**, 776.

acid, the calcium precipitated by the addition of ammonia and ammonium oxalate, and the magnesium determined in the filtrate by precipitation with sodium phosphate (*cf.* p. 406).

4. **Iron** is usually only determined in limestone intended for the manufacture of bleaching powder. Two g. are dissolved in hydrochloric acid, the solution reduced by metallic zinc, diluted, and titrated with permanganate after the addition of manganese sulphate solution free from iron (*cf.* p. 380).

III. LIME

A. QUICK LIME

1. **Free Lime.**—One hundred g. of the average sample are weighed off, carefully slaked, and the resulting cream transferred to a 500 c.c. flask, which is then filled to the mark. One hundred c.c. of the thorougly shaken contents are then drawn off with a pipette and diluted to 500 c.c. in a second flask, and 25 c.c. (= 1 g. quick lime) of the latter well-mixed solution taken for analysis. A small quantity of an alcoholic solution of phenolphthalein is first added and the solution then titrated with normal hydrochloric acid until the red coloration disappears. The colour change takes place when all the free CaO has been neutralised and before the $CaCO_3$ has been attacked. Each 1 c.c. of normal acid = 0·02805 g. CaO. The titration must be effected gradually, and with thorough mixing, otherwise accurate results cannot be obtained (*cf.* p. 72).

C. Stiepel has devised a "lime-calorimeter" for determining the free lime by measuring the heat evolved on slaking. The calculation is based on a liberation of 51500 calories in the combination $CaO + H_2O$. As may be imagined, the results obtained with such an apparatus will not be very exact, and experience has shown that at times they are quite unreliable.

Maynard[1] estimates free caustic lime in admixture with other substances by extracting with pure glycerine at a temperature of 40°. The extraction is continued for five days in a thermostat, and the mixture frequently shaken. The whole is finally filtered at 60° and the lime determined in an aliquot part of the filtrate.

2. **Carbon dioxide.**—The CaO and $CaCO_3$ are titrated together by dissolving the lime in a measured volume of normal hydrochloric acid, and titrating back the excess of acid with normal sodium hydroxide solution. The $CaCO_3$ present can then be calculated by deducting the value found for the CaO under test 1. In very exact work the carbon dioxide should be determined directly as described on p. 149.

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[1] *Bull. Soc. Chim.* 1902 [3], **27**, 851 ; *Chem. News*, 1903, **87**, 109.

B. SLAKED LIME

1. **Water.**—About 1 g. of the substance is weighed off from a stoppered weighing bottle, and gradually heated to a red heat in a platinum crucible; it is then allowed to cool in the desiccator and weighed. The loss in weight = water + carbonic acid.

2. **Carbon dioxide** is estimated as described above (A, No. 2).

3. **Content of milk of Lime in caustic Lime.**—*Blattner's specific gravity method.* In the case of a thin milk, the reading must be made quickly, and before the lime has time to settle out. In the case of thicker milks, the hydrometer is placed gently in the solution, and the containing cylinder slowly rotated, so as to cause gentle shaking, until the hydrometer ceases to sink in the liquor. The cylinder employed should not be too narrow. The following table, reduced from that given by Blattner,[1] gives the relationship between lime content and specific gravity at 15° C.

Degrees Twaddell.	Grams CaO per litre.	Lbs. CaO per cubic foot.	Degrees Twaddell.	Grams CaO per litre.	Lbs. CaO per cubic foot.
2	11·7	0·7	28	177	11·1
4	24·4	1·5	30	190	11·9
6	37·1	2·3	32	203	12·7
8	49·8	3·1	34	216	13·5
10	62·5	3·9	36	229	14·3
12	75·2	4·7	38	242	15·1
14	87·9	5·5	40	255	15·9
16	100	6·3	42	268	16·7
18	113	7·1	44	281	17·6
20	126	7·9	46	294	18·4
22	138	8·7	48	307	19·2
24	152	9·5	50	321	20·0
26	164	10·3	...	...	...

CONTROL OF WORKING CONDITIONS

I. MANUFACTURE OF CHLORINE BY MEANS OF NATIVE MANGANESE ORE

In this process analysis is confined to the determination of the free acid in the manganese liquors coming from the chlorine stills. The quantity of free acid present is determined by simple titration with normal sodium hydroxide solution, the end-point being decided by the appearance of a permanent, flocculent precipitate of ferric hydroxide. The residual acid in a well-finished liquor may be less than 5 per cent. in cases where the stills are heated indirectly; as a rule, the free acid rises to 6 per cent. and over, especially when the heating is done with open steam.

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[1] *Dingl. polyt. J.*, 1883, **250**, 464.

II. The Weldon Process

The finished liquors are examined in the following manner according to Lunge's modification of Weldon's method.

The liquors from the stills are tested for free acid as described above; with recovered manganese, such free acid should not exceed 1 per cent. Occasionally the liquors are also analysed for their manganese content, the method described under Weldon mud being employed (cf. *infra*).

The neutralised and settled liquors are tested for neutrality by means of litmus, and the degree of freedom from suspended matter judged by appearance; the percentage of calcium chloride present is determined by precipitation with oxalic acid in acetic acid solution.[1]

The precipitated mud should further be repeatedly tested during oxidation, as a check on the blowing operation. The method of testing the mud is described below.[2]

The calcium chloride liquors which flow away from the settled mud are examined for freedom from mud carried forward mechanically.

The mud obtained from the settling-tanks or filter-presses must be examined for both soluble and insoluble manganese.

Hydrochloric acid used in the Weldon process should be as free as possible from sulphuric acid.

The Examination of Weldon Mud.

1. Manganese dioxide. — For this determination a standard acid solution of ferrous sulphate is required. It is prepared by dissolving 100 g. of crystallised ferrous sulphate and 100 c.c. of concentrated pure sulphuric acid in 1 litre of water (*cf.* p. 103), and is standardised by diluting 25 c.c. with 100 to 200 c.c. of cold water and titrating with $N/2$ potassium permanganate solution, until the rose coloration remains permanent for at least half a minute. The ferrous sulphate solution gradually changes in value, and must therefore be checked from day to day.

The mud must be thoroughly shaken before testing (mere stirring is not sufficient), and 10 c.c. drawn off with a pipette immediately and before any settling has occurred. The outside of the pipette is freed from mud by washing, and the 10 c.c. of mud allowed to flow into 25 c.c. of the ferrous sulphate solution contained in a beaker, any particles adhering to the inner walls of the pipette being washed into the beaker by the aid of a wash-bottle. The mixture is then shaken until all the mud has dissolved, 100 c.c. of water added, and the solution titrated with permanganate. If the 25 c.c. of acid ferrous sulphate solution required x c.c. of permanganate, and the 10 c.c. of the mud and ferrous

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 350.

[2] Cf. *ibid.*, p. 353.

sulphate y c.c. of permanganate, then $2{\cdot}175\ (x-y)$ gives the number of grams of MnO_2 present in 1 litre of the mud, and $2{\cdot}175(x-y) \times 0{\cdot}0624$ the number of pounds per cubic foot.

2. **Total Manganese.**—Ten c.c. of the mud are measured off, observing the precautions described under test 1, and boiled with strong hydrochloric acid until chlorine ceases to be evolved. The excess of acid is then neutralised by addition of powdered marble or precipitated calcium carbonate, a strong filtered solution of bleaching powder added, the whole boiled for a few minutes until the colour becomes deep red, taking care that the mixture still smells of bleaching powder, when alcohol is added drop by drop until the red colour is destroyed. The whole of the manganese is then present as peroxide, which is filtered off and washed. The filtrate should be tested for freedom from manganese by adding bleaching powder solution, when no brown coloration should result. Washing is continued until the washings cease to give a reaction with iodised starch paper. The filter paper and precipitate are then thrown into 25 c.c. of standard ferrous sulphate solution, and dissolved by stirring as above. Should any of the manganese dioxide remain undissolved, a further 25 c.c. of the ferrous sulphate solution is added. The solution is diluted with 100 c.c. of water, and titrated with permanganate, the results being calculated as under test 1, and expressed as MnO_2 per litre or per cubic foot.

3. **The "Base,"** that is, the monoxides in the mud which neutralise hydrochloric acid but do not liberate chlorine. It may contain lime, magnesia, ferrous oxide, and manganous oxide.

Ten c.c. of the well-shaken mud are added from a pipette to 25 c.c., or 50 c.c. in the case of a very high base, of normal oxalic acid solution (63 g. cryst. oxalic acid per litre), previously diluted to about 100 c.c. and warmed to a temperature of 60° to 80°, and the mixture well stirred until the precipitate ceases to appear yellow and becomes pure white. This should not take long, if the operation is carried out at the temperature specified. The solution is diluted to 202 c.c. (2 c.c. representing the volume occupied by the precipitate) in a suitably marked 200 c.c. flask, filtered through a dry pleated filter paper, and 100 c.c. titrated with normal sodium hydroxide solution. Tincture of litmus or phenolphthalein must be used as the indicator, since methyl orange cannot be employed with oxalic acid (*cf.* p. 65). The oxalic acid taken up by the mud serves (1) to reduce the MnO_2 to MnO with liberation of carbon dioxide; (2) to combine with and neutralise the manganous oxide so formed; (3) to saturate the monoxides, including manganous oxide originally present, that is, the "base." The quantities taken up under 1 and 2 are equal, and the two together have the same value as the MnO_2 as determined in test 1, and so equal $x-y$, since the oxalic acid solution is normal, whilst the permanganate solution is only semi-normal. If z c.c. of normal sodium hydroxide are used in titrating back the excess of oxalic acid, the substances under 3 correspond to the oxalic acid originally taken, 25 (or 50) c.c. less $x-y$ and $2z$; therefore this value $w=25$ (or $50)-(x+2z)+y$. By the term "base" is understood the ratio between the value for the substances under 3, expressed by w, and the value for 1, expressed by $\frac{x-y}{2}$ (the sodium hydroxide solution being normal and the permanganate semi-normal); this ratio therefore equals $\frac{2w}{x-y}$. When 25 c.c. oxalic acid solution are used, it becomes:—

$$\frac{50-2x-4z+2y}{x-y} = \left(\frac{50-4z}{x-y}\right)-2,$$

or, when 50 c.c. oxalic acid are taken $= \left(\frac{100-4z}{x-y}\right)-2.$

III. The Deacon Process

In this process the ratio between hydrochloric acid gas and air must be determined both in the gases leaving the saltcake pot, and also in the gases leaving the Deacon decomposer.

In the case of the gases from the saltcake pot it suffices to determine the volume percentage of hydrochloric acid gas present, as the residual gas is essentially air. This is effected by aspirating the gases through a measured volume of sodium hydroxide solution of known strength, coloured with litmus or methyl orange until the indicator changes colour; the volume of non-absorbed gas (air) is ascertained by measuring the water which has run from the aspirator. Since the ratio of the volume of hydrochloric acid gas to the sodium hydroxide solution used is constant, and the volume of the air is given by the water collected, the ratio between the acid and the air is easily calculated. The principle of the method and the apparatus employed are the same as those described under Lunge's modification of Reich's method for the analysis of kiln gases (p. 299).

The gases leaving the decomposer are tested, as a rule, for free chlorine and for unchanged hydrochloric acid, and occasionally also for water vapour and for carbon dioxide.

1. Ratio between the free Chlorine and the unchanged Hydrochloric acid gas.—*Decomposition value.* Simple absorption of the gases in sodium hydroxide solution followed by titration for available and total chlorine is not applicable in this case, since it is impossible to avoid the formation of chlorate.[1] This difficulty has been overcome by the following method, devised in the works of Messrs Gaskell, Deacon, & Co.

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[1] *Cf.* C. Winkler, *Industrie Gase*, vol. ii., p. 318.

Five litres of the gas leaving the decomposer are aspirated through 250 c.c. of sodium hydroxide solution of sp. gr. 1·075, divided between two or three bottles, to absorb both the hydrochloric acid gas and the chlorine. The apparatus should be fixed as near to the decomposer as possible, and the time during which the gas sample is taken should correspond with the period of working a charge through the saltcake pot. The contents of the several absorption bottles are united, diluted to 500 c.c., and tested as follows:—

1. One hundred c.c. of the solution are heated to boiling with 25 c.c. of the acid ferrous sulphate solution, prepared and standardised as described in p. 478, in a flask provided with a Contat bulb (Fig. 39, p. 106). When cold, the contents of the flask are diluted with 200 c.c. of water, and titrated with $N/2$ permanganate solution. Let y represent the number of c.c. so required and x the number of c.c. of permanganate necessary to oxidise the 25 c.c. of ferrous sulphate solution.

2. A small volume of sulphur dioxide solution is added to 10 c.c. of the above alkaline solution and the mixture acidified with dilute sulphuric acid, so that there is a distinct smell of sulphur dioxide. The acidified solution is heated to boiling, allowed to cool, a few drops of permanganate solution added, if necessary, to oxidise any remaining sulphurous acid, after which the solution is neutralised with pure sodium carbonate diluted with water and titrated with $N/10$ silver nitrate solution, employing neutral potassium chromate as indicator. Let z stand for the number of c.c. silver nitrate solution required. The percentage decomposition of the hydrochloric acid gas is then given by the expression $50\frac{(x-y)}{z}$, and the volume of air per 1 volume HCl by $\frac{43{\cdot}53+\frac{x-y}{8}}{z}$. Should some other volume of gas, n, be aspirated instead of the 5 litres, the constant, 43·53, must be altered to $\frac{1{\cdot}624n}{50 \times 0{\cdot}003645}$, assuming that the remaining operations are carried out exactly as above, and that 1 litre HCl at 50° and 760 mm. pressure weighs 1·624 gram.

Younger[1] passes the gas through a solution of arsenious acid and employs an aspirator which gives the weight of chlorine in unit volume of the gases directly. The percentage of hydrochloric acid in the gas is determined by titrating the resulting solution with silver nitrate. The absorption is effected in a cylinder containing 100 c.c. of an aqueous solution of arsenious acid, each 1 c.c. of which corresponds to 0·15432 grains (=0·01 g. chlorine). The charged cylinder is connected with the bottle B (Fig. 140), containing about 1 g. potassium iodide dissolved in water; the arsenious acid solution is coloured blue by a very small quantity of indigo-carmine.

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[1] *J. Soc. Chem. Ind.*, 1889, **8**, 88.

A cubic foot (0·0283 cub. m.) in capacity of the aspirator C is divided into any convenient number of parts; for example, 112. One side of the gauge glass D is calibrated to give the grains of chlorine per cubic foot of gas, and the corresponding volume of gas aspirated is given on the other side of the same lines. The liberation of iodine from the potassium iodide solution and the simultaneous bleaching of the indigo-carmine indicate the completion of the test, and when this occurs the aspiration is interrupted and the readings taken. Thus, for example, if the mark E represents 1 cubic foot and the water stands at this level on the completion of the test, the readings indicate that 1 cubic foot of the gas contains 15·432 grains of chlorine. Should the water-level stand at the ½ cubic foot mark, the presence of 30·864 grains chlorine per cubic foot of gas is indicated by the scale, and so on.

The hydrochloric acid is determined by titrating 10 c.c. of the arsenious acid solution with $N/10$ silver nitrate solution. Should the gases be free from hydrochloric acid the silver nitrate necessary for titration will be 28·2 c.c., this volume corresponding to the hydrochloric acid derived from the chlorine absorbed. Any volume over and above this 28·2 c.c. corresponds to the hydrochloric acid present as such in the gases.

The iodine liberated in the potassium iodide bottle generally indicates about 0·2 to 0·3 grains of chlorine. The potassium iodide bottle is not necessary as an indicator for the completion of the reaction; its main function is to show that the aspiration is not carried out too rapidly, and that no chlorine passes unabsorbed through the arsenious acid solution.

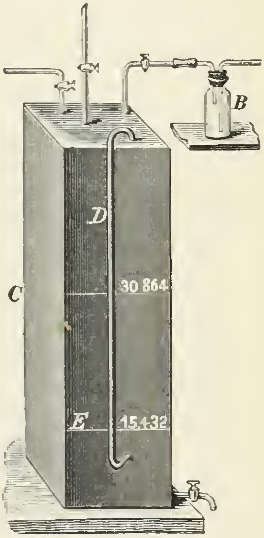

FIG. 140.

In a subsequent communication[1] Younger gives the following particulars for the analysis of Deacon gases: A measured volume of the gas is drawn first through weighed bottles containing concentrated sulphuric acid, the gain in weight giving the moisture present; secondly, through a tube containing a solution of arsenious acid, to arrive at the chlorine and hydrochloric acid content, as above; and finally, through an apparatus in which the oxygen may be absorbed and measured.

The following example, showing the methods of calculating the results, is taken from Winkler,[2] the data for the gases being corrected to the real litre weights. The free chlorine was determined by an arsenious acid solution, of which 1 c.c. = 0·0025 g. Cl, and the total

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[1] *J. Soc. Chem. Ind.*, 1890, 9, 159.

[2] *Industrie Gase*, vol. ii., p. 317.

chlorine by a silver nitrate solution, of which also 1 c.c. $= 0{\cdot}0025$ g. Cl. The following volumes of these solutions were consumed per litre of unabsorbed gas. Fifty c.c. arsenious acid solution $= 50 \times {\cdot}0025 = 0{\cdot}125$ g. free chlorine, and 100 c.c. silver nitrate solution $= 100 \times 0{\cdot}0025 = 0{\cdot}25$ g. total chlorine. The extent of the decomposition is given by the equation :—

$$0.250 : 0.125 = 100 : x,$$
$$x = 50,$$

or a 50 per cent. decomposition had been effected. These two determinations thus give the decomposition value and the ratio between the chlorine and hydrochloric acid present in the gas.

Should it be desired to ascertain the volume percentage of the two gases leaving the Deacon decomposer, it is necessary to calculate to c.c. the ascertained weight of free chlorine, and of hydrochloric acid. One c.c. Cl $= 0{\cdot}003219$ g., consequently the $0{\cdot}125$ g. Cl found correspond to $40{\cdot}2$ c.c. Cl, which is the volume present per 1 litre of non-absorbable gas.

To calculate the volume of the hydrochloric acid present, since its weight corresponds to half that of the total chlorine in the gases, it is,

$$= \frac{0.250}{2} = 0.125 \text{ g. Cl} = 0.1285 \text{ g. HCl.}$$

One c.c. HCl weighs $0{\cdot}001641$ g.; therefore :—

$$0{\cdot}1285 \text{ g.} = 78{\cdot}3 \text{ c.c. HCl}$$

per litre of non-absorbable gas. The *gas leaving the decomposer* thus possesses the following composition :—

1000 c.c. oxygen and nitrogen,
78·3 „ hydrochloric acid gas,
40·2 „ chlorine ;

or, expressed in percentages by volume :—

89·40 vol. per cent. oxygen and nitrogen,
7·00 „ „ hydrochloric acid gas,
3·60 „ „ chlorine.

2. **The percentage by volume of Hydrochloric acid gas in the gases before entering the decomposer** is arrived at from the total chlorine as follows.

The total chlorine found, namely 0·250 g., corresponds to 0·257 g. or 156·6 c.c. HCl. Consequently the gases entering the decomposer correspond to :—

1000.0 c.c. air,
156.6 c.c. HCl,

which gives 13·60 volume per cent. HCl.[1]

It is usual to simplify the calculations as far as possible, and such

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[1] This leaves out of account the oxygen which has interacted with the HCl, and assumes that there is no leakage into the decomposer (Conroy).

simplification does not affect the result to any great extent. For example, the weight of 1 c.c. chlorine may be rounded off to 0·0032 g., and that of 1 c.c. HCl gas to 0·0016, thus saving trouble in calculating the inactive chlorine to hydrochloric acid; that is, the weight of 1 c.c. HCl is taken to be one-half that of 1 c.c. of chlorine. If these simplifications be introduced in working out the above example, the following values are obtained :—

For the Gases leaving the Decomposer.

$$\frac{0.125 \text{ g. active chlorine}}{.0032} = 39.06 \text{ c.c.} = 3.49 \text{ vol. per cent. (instead of } 3.60)$$

$$\frac{0.125 \text{ g. inactive chlorine}}{.0016} = 78.12 \text{ c.c.} = 6.99 \text{ vol. per cent. (instead of } 7.004)$$

For the Gases entering the Decomposer.

$$\frac{0.250 \text{ g. total chlorine}}{0.0016} = 156.25 \text{ c.c.} = 13.51 \text{ vol. per cent. HCl (instead of } 13.60).$$

It is unnecessary to make any corrections for temperature and pressure, since the errors from this source are throughout essentially of the same magnitude, and the results obtained are therefore sufficiently comparable.

3. **Carbon dioxide.**—The estimation of this gas is important in the examination of Deacon gases, since the presence of any appreciable amount in the chlorine renders the production of high-strength bleach impossible.

Hasenclever's method[1] of estimation consists in passing a measured volume of the gas (previously freed from hydrochloric acid by bubbling through a wash-bottle containing water) through an ammoniacal solution of barium chloride. After the absorption is complete the solution is heated, the barium carbonate filtered off and thoroughly washed with boiled water. The washed precipitate is then either ignited and weighed, or dissolved in hydrochloric acid and converted into barium sulphate. The weight of carbon dioxide in the gas is calculated from the weight of precipitate obtained (1 g. $BaSO_4 = 0{\cdot}1885$ g. CO_2), and compared with the volume of gas, say 20 litres, collected in the aspirator.

According to Sieber,[2] this method is only applicable to dilute gases containing not more than 10 per cent. of chlorine, a condition always satisfied by Deacon gases. In the case of more concentrated gases, such as electrolytic chlorine, which may contain carbon dioxide arising from the carbon electrodes used, the method is unsuitable, owing to the solubility of barium carbonate in barium chloride. The object of boiling the solution before filtering off the barium carbonate is to destroy any carbamate present in the liquors. It is also possible to determine the

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[1] *Cf.* Winkler, *loc. cit.*, p. 368.

[2] *Chem. Zeit.*, 1895, 19, 1963.

carbon dioxide by absorbing the gases with sodium hydroxide solution, destroying the sodium hypochlorite formed by addition of sodium arsenite, and then liberating the carbon dioxide by means of sulphuric acid. This method is, however, inconvenient, since it necessitates a previous determination of the carbon dioxide in the various reagents employed; it is also uncertain, when only small amounts of carbon dioxide are present. A better plan is to absorb the gases in sodium hydroxide solution of known carbonate content, to decompose the sodium hypochlorite by boiling with cobalt oxide, and then to decompose with sulphuric acid, passing the liberated carbon dioxide through a solution of potassium iodide previously saturated with carbon dioxide and air, to retain any traces of chlorine carried forward. The purified gas is then collected in a cooled potash bulb, and weighed.

In this connection Lunge[1] remarks that the gas must, of course, be dried beforehand, and that the process, in addition to being very complicated, is quite unreliable for the determination of small quantities of carbon dioxide, especially on account of the necessity of working with a solution of potassium iodide saturated as above. It is both simpler and more accurate to absorb the gas in sodium hydroxide solution, to decompose the hypochlorite completely by boiling with ammonia, and then to estimate the carbon dioxide in the ordinary way either by liberating the gas (p. 149) or by the barium chloride method (p. 72).

Treadwell[2] makes use of the burette shown in Fig. 141, for estimating the carbon dioxide in electrolytic chlorine. The burette is of the Bunté type, and is provided with a levelling tube. The capacity of the burette, from tap to tap, must be accurately determined, the most suitable capacity being 100 c.c. The burette B should be thoroughly dried before making a determination, and the chlorine gas to be examined should, after drying by passing through a calcium chloride tube, be allowed to flow through the burette for from five to ten minutes before closing the taps. At the end of this time the lower three-way tap *a* is closed, then the upper two-way tap *b*, and the temperature and barometric height noted. The lower tap is then connected by the rubber tube to N, which is filled with a 5 per cent. solution of sodium hydroxide; *a* is then turned so as to connect N with the outside air, as shown in the figure. As soon as the liquid flows through the tap, the latter is closed,

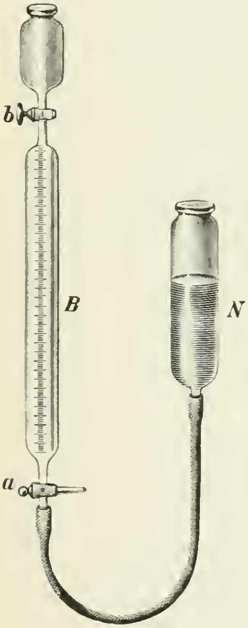

Fig. 141.

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[1] *Handbuch der Sodaindustrie*, vol. iii., p. 698.

[2] *Analytical Chemistry*, vol. ii., p. 614.

N raised, and the tap *a* turned so as to allow a little of the solution to enter B. The tap *a* is then closed, and the burette suitably inclined so that its walls are thoroughly wetted with the solution; this promotes the rapid absorption of the chlorine and carbon dioxide. The opening and closing of the tap *a* and the movement of the burette is repeated several times until absorption is complete. When all the chlorine and carbon dioxide have been absorbed, the tubes B and N are adjusted to the same level, and the volume of unabsorbed gas (oxygen, nitrogen, carbon monoxide) read off. As a rule, the residue only amounts to from 0·5 to 1 per cent.

To estimate the chlorine, the funnel on the top of the burette is first washed out with water, in order to remove any small quantity of chlorine that may remain from the introduction of the sample, the tap *a* closed, and the solution in N run out into a beaker through the side connection of *a*; N and the rubber tubing are then disconnected and washed out. The contents of the burette are transferred to the same beaker and the burette well washed with water, added through the funnel. The absorbed chlorine is titrated with arsenious acid. One hundred c.c. $N/10$ sodium arsenite solution are added (this quantity will always be found sufficient), then phenolphthalein, followed by hydrochloric acid till the red colour first disappears, and the excess of arsenite solution determined by titration with $N/10$ iodine solution, starch solution being used as indicator. The number of c.c. of chlorine in the gas, measured dry at 0° and 760 mm., are obtained by multiplying the number of c.c. of arsenite solution consumed by 1·1015. The value so obtained must be recalculated, to give the volume at the temperature and pressure at which the gas was measured. The carbon dioxide is obtained as the difference between the chlorine and the total gas absorbed.

This method is subject to the error that appreciable quantities of chlorate are formed in the absorption of the chlorine, and the results are always from 0·7 to 0·77 per cent. too low.[1] Treadwell and Christie[2] have accordingly modified the process by first absorbing the chlorine with an alkaline arsenite solution free from carbonate, and then the carbon dioxide by alkali hydroxide. The arsenite solution is made by dissolving 4·95 g. of arsenious oxide in dilute potassium hydroxide solution, adding phenolphthalein, exactly neutralising with sulphuric acid, and diluting to 1 litre. One hundred c.c. of this $N/10$ solution are introduced into the burette through the tap *a*, for the absorption, and subsequently 10 c.c. of a 1 : 2 potassium hydroxide solution through the funnel above *b*. After taking the readings, the solutions and washings are collected, phenolphthalein added, and the whole neutralised with hydrochloric acid; 60 c.c. of sodium bicarbonate solution (40 g. per litre)

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[1] *Z. angew. Chem.*, 1905, 18, 1930.

[2] *Ibid.*

are then introduced, and the excess of arsenite solution titrated with $N/10$ iodine solution and starch. One c.c. $N/10$ solution = 0·003545 g. Cl, or 1·1015 c.c. N.T.P. The carbon dioxide is determined by difference, as above.

Correct results may also be obtained if two samples of the gas are taken at the same time in a couple of Bunté burettes arranged in series, the gas in the first being treated with sodium hydroxide solution as above, and that in the second with a solution of potassium iodide, and the chlorine estimated by titrating the liberated iodine with standard arsenite or thiosulphate solution. Each 1 c.c. $N/10$ solution required corresponds to 0·003545 g., or 1·1015 c.c. dry chlorine measured at 0° and 760 mm. The volume under these conditions is calculated to the volume under the conditions of analysis by means of the formula $\frac{760(273+t)}{(b-f)273}$ where f stands for the tension of aqueous vapour at the temperature $t°$; or the Tables VI., VII., and VIII. (Appendix) may be used. The carbon dioxide is arrived at as the difference between the volumes absorbed in the two burettes. It can also be determined directly in a single burette by introducing exactly 45 c.c. $N/5$ sodium hydroxide solution the carbonate in which has been determined, as described below (p. 514). These 45 c.c. are placed in the funnel of the burette after the sample has been collected, and as much as possible allowed to enter the burette; the whole is then shaken. From 5 to 10 c.c. of a neutral 3 per cent. solution of hydrogen peroxide are added to decompose the sodium hypochlorite, the burette again shaken, the contents run into a 200 c.c. flask, the burette well washed with water free from carbon dioxide, and the solution made up to 200 c.c. Fifty c.c. of this solution are taken for the determination of the carbon dioxide which may be carried out very accurately by the Lunge and Marchlewski method (p. 149), or sufficiently accurately, for most purposes, by adding sodium chloride and phenolphthalein and titrating with $N/5$ hydrochloric acid at a temperature slightly above 0°.[1]

Treadwell and Christie[2] have modified this method as follows:—The chlorine is absorbed by a 5 per cent. solution of potassium iodide, then the carbon dioxide by 10 c.c. of potassium hydroxide solution, and the total volume of absorbed gas determined. The excess of hydroxide converts the liberated iodine into iodide and iodate. The liquid from the apparatus is then run into a beaker containing 10 c.c. of strong hydrochloric acid, when the iodine is again liberated, and is titrated with thiosulphate. The results are accurate, but the method presents no advantage over the arsenite method as described above.

Lunge and Rittener[3] absorb the chlorine in a Bunté burette with

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[1] *Cf.* Offerhaus, *Z. angew. Chem.*, 1903, **16**, 1033.

[2] *Ibid.*, 1905, **18**, 1930.

[3] *Z. angew. Chem.*, 1906, **19**, 1853.

an $N/10$ solution of sodium arsenite and then the carbon dioxide with sodium hydroxide; the unchanged arsenite is titrated back and the carbon dioxide obtained by difference from the volume of total absorbable gases found. The details of the method are given on p. 514

The above methods are of considerable importance in the analysis of electrolytic chlorine. Nourisson[1] examines such chlorine in an Orsat apparatus by first absorbing the chlorine by stannous chloride, then the carbon dioxide by a solution of sodium hydroxide, and finally the oxygen by metallic copper and ammonia solution. Schloetter[2] absorbs the chlorine by hydrazine sulphate, each 2 volumes of chlorine absorbed liberating 1 volume of nitrogen, and subsequently the carbon dioxide by sodium hydroxide solution.

4. **Moisture** in the Deacon gases may be determined when necessary by inserting a U-tube filled with pumice moistened with concentrated sulphuric acid, or a bulb apparatus containing sulphuric acid, between the gas main and the absorbing bottle for the chlorine and hydrochloric acid, and determining the gain in weight. It is essential to drive all chlorine and hydrochloric acid gas out of the absorbing tube before weighing, by passing a current of dry air through the U-tube for a sufficient time; also it is advisable to insert a second weighed sulphuric acid tube behind the drying apparatus during the operation.

IV. THE MANUFACTURE OF BLEACHING POWDER

The method of examining the lime used in filling the chambers has already been described (p. 484). The main point to be attended to in the manufacturing operation is the strength of the bleach, which must be brought to a specified standard. This is controlled by analysis; the various methods available are described under "Finished products" (p. 499). It is, of course, essential that the sample drawn from the chamber should be representative of the bulk.

The chambers must not be opened until it has been ascertained that this may be done with safety to the workmen, and without giving rise to undue nuisance.[3] Before the chamber is opened, the chlorine present in the gas space must not exceed 5 grains per cubic foot (= 11·5 g. per cubic metre); this limit was agreed to by manufacturers about twenty years ago, but the present practice is to restrict the limit to 2½ grains per cubic foot.

The determination of the chlorine present in the chamber atmosphere may be carried out in an Orsat apparatus, the simplified form described by Fleming-Stark,[4] Fig. 142, being especially suitable.

The burette *a* is filled with water and connected by means of a

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[1] *Chem. Zeit.*, 1904, **28**, 107.

[2] *Z. angew. Chem.*, 1904, **17**, 301.

[3] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 458.

[4] *J. Soc. Chem. Ind.*, 1885, 4, 311.

rubber tube with the reservoir *b*, a tap *c* being inserted between the two. This tap is provided with two passages at right angles to each other, the one of small and the second of large diameter. This arrangement allows of a strong flow of water when filling the burette, and of a diminished flow when the gas is forced into the absorbing solutions.

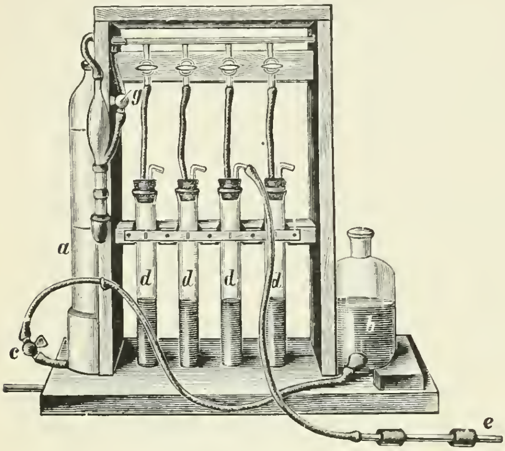

FIG. 142.

The four tubes *d* are filled with an aqueous solution of potassium iodide, and each may be connected through a corresponding glass tap with the burette. Each absorption tube is provided with a double-bored stopper, and a tube reaching almost to the bottom of the absorption vessel passes through one of these openings. This tube is narrowed at its lower end, so as to break up the gas-bubbles entering the absorbing solution, and at its upper end is connected through the tube *e* with the bleaching powder chamber. The tube passing through the second opening in the stopper is cut off just below the stopper, and serves to connect the absorbing vessels with the burette. A small wash-bottle containing potassium iodide solution and starch is inserted between the absorption tubes and the burette. The two-way tap *g*, provided between the wash-bottle and the burette, permits the air to escape during the filling of the burette without passing through the wash-bottle.

In using the apparatus, 387·7 c.c. of gas, as measured in *a*, are drawn through one of the absorption tubes *d*; the solution in the wash-bottle affords an absolutely safe indication of the completeness of the chlorine absorption. The contents of *d* are then washed into a beaker, and titrated with $N/10$ sodium arsenite solution. The grains of chlorine per cubic foot are obtained by multiplying by 2 the number of c.c. of arsenite solution so required.

The Government inspectors make use of the simple apparatus shown in Fig. 143.[1] A is an ordinary rubber pressure ball of about 100 c.c. capacity, provided with a small hole, B, in the mouthpiece. The end of the mouthpiece passes through one of the two holes in the cork C, a glass tube, D, bent at right angles passing through the second. This latter tube reaches nearly to the bottom of the cylinder E, and is

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[1] Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 458.

narrowed down at the lower end, so that only a very fine needle can be inserted. The cylinder E is filled with the solution described below, and the outer end of D is inserted in an opening in the bleach chamber at a height of 2 feet above the floor. To take a sample of the chamber gas, A is compressed, the hole B being covered by the finger, and the pressure then released; by the expansion of the bulb the gas in the chamber is drawn through the tube D and the solution in E. The operation is repeated until the solution in E becomes coloured through separation of iodine, and the number of aspirations required to cause this is noted. Each delivery of the bulb corresponds to 4 ozs. (about 100 c.c.), or $\frac{1}{250}$ of a cubic foot. The solution employed is prepared by dissolving 0·3485 g. of arsenious acid in sodium carbonate, neutralising with sulphuric acid, adding 25 g. of potassium iodide, 5 g. of precipitated calcium carbonate, 6 to 10 drops of ammonia, and diluting the whole to 1 litre. Twenty-six c.c. of this solution are employed for each test, and a little starch solution is added as indicator. Under these conditions five deliveries of the bulb will produce a coloration when the gas contains 5 grains of chlorine per cubic foot, ten deliveries when the chlorine content is only 2$\frac{1}{2}$ grains per cubic foot, and so on.

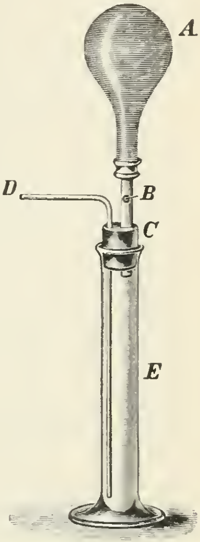

FIG. 143.

V. THE MANUFACTURE OF POTASSIUM CHLORATE

In the old process of manufacture, in which a warm solution of milk of lime is treated with chlorine, the methods of examining the lime and milk of lime are those already described (p. 484). The resulting liquor must be examined for its content of chlorate, since this is the basis on which the potassium chloride necessary for conversion into chlorate is calculated, and further for the percentage of calcium chloride present, as a check on the working of the process.

Determination of the Chlorate.—Two c.c. of the liquor are measured off with an accurate pipette and boiled, after the addition of a little hot water and a drop of alcohol, to remove any dissolved free chlorine. A flask fitted with a Bunsen valve or Contat bulb (Fig. 39, p. 106) is used for the test, but the valve is not inserted during the above preliminary heating. The complete removal of chlorine is indicated by the disappearance of all smell of chlorine and of the red colour. The flask and contents are allowed to cool, 25 c.c. of the acid ferrous sulphate solution (corresponding to a c.c. $N/2$ permanganate solution) described on p. 485, added, the whole boiled for ten minutes, and the valve inserted. When cold, the solution is titrated with $N/2$ permanganate solution, b c.c., say, being necessary to produce the coloration. The chlorate contained in 1 litre of the liquor will then be 5·105 $(a-b)$ g. calculated as $KClO_3$, and the potassium chloride theoretically necessary to convert the calcium into the potassium salt will be 3·106 $(a-b)$ g. per litre.[1]

The chlorate remaining in the mother liquors is similarly determined.

The chlorate may also be determined by Bunsen's method, namely, boiling with strong hydrochloric acid and absorbing the liberated chlorine in a solution of potassium iodide; the method is, however, no more advantageous in this case than in that of manganese ore (p. 478).

Rasenack[2] describes a method which consists in precipitating the chloride present by addition of silver nitrate, reducing the chlorate in the filtrate by means of zinc, and titrating the resulting chloride. This method is much more troublesome than the above, and the same may be said of all other reduction methods depending on the estimation of the chloride produced. An iodometric method has been proposed by de Koninck and Nihoul.[3]

Other methods for the determination of chlorates are described on p. 511.

Calcium chloride.—The chloride (calcium chloride) in the liquors is estimated as follows:—1 c.c. of the liquor is treated as above, to destroy free chlorine, until the red colour disappears, a little neutral potassium chromate added, and the solution titrated with $N/10$ silver nitrate solution, as described on p. 123. Each 1 c.c. of the silver nitrate solution corresponds to chlorine equivalent to 7·46 g. KCl per litre.

Should it be necessary to determine the *free Chlorine* and *Hypochlorite* present in the liquor, a measured volume of the latter is allowed to flow into an excess of potassium iodide solution and the iodine liberated determined by titration with thiosulphate. It is not permissible to add sodium carbonate to fix the chlorine before adding the potassium iodide, since, owing to the formation of iodic acid and to the oxidation of the thiosulphate, too much iodine is then required.[4] The "bleaching-chlorine" may, however, according to Pontius, be titrated directly with potassium iodide solution after addition of sodium bicarbonate (*cf.* p. 503).

The titration may also be carried out by Penot's method, described under bleaching powder, by addition of sodium arsenite solution, until a drop of the titrated liquor ceases to produce a blue colour on potassium iodide starch paper; or the arsenite solution may be added in excess and titrated back with iodine solution.

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[1] *Cf.* also, Rosenbaum, *Z. angew. Chem.*, 1893, **6**, 80.

[2] Dammer, *Lexikon der Verfälschungen*, p. 423.

[3] *Z. angew. Chem.*, 1890, **3**, 77.

[4] Friedheim, *Z. anorg. Chem.*, 1893, **4**, 145.

FINISHED PRODUCTS

I. Bleaching Powder

Owing to the unstable nature of this substance, very special attention must be given to the collection and preservation of the samples. Exposure to air and to daylight is very prejudicial; exposure to sunlight still more so. The samples are drawn from the separate casks by a suitable auger (p. 13), and placed one after the other in a wide-mouthed bottle, which must be closed immediately after each portion has been introduced. The mixing and filling into the separate sample bottles, together with the sealing up of the latter, is performed as rapidly as possible in the manner prescribed on p. 11. The samples must be kept in a cool, dark place prior to testing, and the tests should be made without delay.

The technical analysis of bleaching powder is confined to the determination of the "available" or "bleaching" chlorine, that is, to the compound $CaCl(OCl)$ which splits up into $Ca(OCl)_2$ and $CaCl_2$ on solution in water, and consequently shows the reactions of a hypochlorite. The quantity of available chlorine present is, in England and America, always expressed as percentage by weight on the bleaching powder, and the same method is usually followed in Germany and most other countries. In France, however, and to a certain extent in other countries, the strength is quoted in terms of Gay-Lussac degrees, which indicate the number of litres of chlorine gas, reduced to 0° and 760 mm., capable of being evolved from 1000 g. of bleaching powder. The following table shows the relationship between the English and French degrees.

French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.
63	20·02	77	24·47	91	28·92	105	33·36	119	37·81
64	20·34	78	24·79	92	29·23	106	33·68	120	38·13
65	20·65	79	25·10	93	29·55	107	34·00	121	38·45
66	20·97	80	25·42	94	29·87	108	34·32	122	38·77
67	21·29	81	25·74	95	30·19	109	34·64	123	39·08
68	21·61	82	26·06	96	30·51	110	34·95	124	39·40
69	21·91	83	26·37	97	30·82	111	35·27	125	39·72
70	22·24	84	26·69	98	31·14	112	35·59	126	40·04
71	22·56	85	27·01	99	31·46	113	35·91	127	40·36
72	22·88	86	27·33	100	31·78	114	36·22	128	40·67
73	23·20	87	27·65	101	32·09	115	36·54	...	...
74	23·51	88	27·96	102	32·41	116	36·86	...	...
75	23·83	89	28·28	103	32·73	117	37·18	...	...
76	24·15	90	28·60	104	33·05	118	37·50	...	...

The following table, prepared by Lunge and Bachofen,[1] gives the

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[1] *Z. angew. Chem.*, 1893, 6, 326.

available chlorine corresponding to various specific gravities of bleaching powder solutions.

Specific Gravity at 15°.	Available Chlorine. Grms. per litre.	Specific Gravity at 15°.	Available Chlorine. Grms. per litre.	Specific Gravity at 15°.	Available Chlorine. Grms. per litre.
1·1155	71·79	1·0800	49·96	1·0350	20·44
1·1150	71·50	1·0750	45·70	1·0300	17·36
1·1105	68·40	1·0700	42·31	1·0250	14·47
1·1100	68·00	1·0650	39·10	1·0200	11·41
1·1060	65·33	1·0600	35·81	1·0150	8·48
1·1050	64·50	1·0550	32·68	1·0100	5·58
1·1000	61·50	1·0500	29·60	1·0050	2·71
1·0950	58·40	1·0450	26·62	1·0025	1·40
1·0900	55·18	1·0400	23·75	1·0000	Trace
1·0850	52·27	...	...	...	...

Very many methods[1] have been devised for the estimation of the available chlorine in bleaching powder, of which the following are the most important.

Gay-Lussac's Arsenious acid method.—This, the oldest method, was introduced by Gay-Lussac in 1835, and is still in general use in France. It consists in treating the bleach with a hydrochloric acid solution of arsenious acid, prepared by dissolving 4·409 g. of arsenious acid in hydrochloric acid, and diluting with water to 1 litre. Ten c.c. of this solution are rendered blue by the addition of a drop of indigo solution, and titrated with a solution of bleaching powder until the blue colour disappears. The bleach solution is prepared by rubbing 10 g. of the bleaching powder with water and diluting to 1000 c.c. Since 0·04409 g. As_2O_3 corresponds to 10 c.c. of chlorine gas measured at 0° and 760 mm., it is only necessary to divide the number of c.c. of the bleach solution required to decolorise the indigo solution into 1000, to obtain the number of litres of chlorine gas corresponding to 1 kilo of bleach. The method is, however, very inexact, and the results obtained vary considerably, according to the degree of dilution and the excess of acid present. Chlorine and arsenious acid can exist side by side in dilute solutions, and consequently the bleaching of the indigo is no indication that all arsenious oxide has been oxidised. Further, the indigo is always partially decolorised where the bleach solution enters the arsenious acid solution, so that the coloration gradually becomes weaker as the titration proceeds, thus causing the end-reaction to be very indistinct.

On account of this gradual decolorisation, Denigés[2] replaces the indigo sulphate by potassium bromide, the end of the titration being indicated by the appearance of a distinct yellow colour. This indicator is also,

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[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 429.

[2] *J. Pharm. Chim.*, 1891 [5], **23**, 101.

according to Denigès, very suitable for titrating commercial hypochlorite solutions (Eau de Javel) when these are coloured pink through presence of permanganate. In this case the small amount of permanganate present is first decomposed by the arsenious acid solution. The estimation is carried out in the usual manner by adding a few drops of concentrated potassium bromide solution to 10 c.c. of the bleach solution, and titrating the arsenious acid with this solution until a permanent faint yellow coloration is obtained.

Graham's Ferrous sulphate method.—This method, formerly in general use in England and Germany, is no more accurate than the above and is, moreover, distinctly inconvenient to carry out. It depends on the oxidation of ferrous salts by bleaching powder in acid solution. 3·9 g. of crystallised ferrous sulphate, $FeSO_4 7H_2O$, which require for complete oxidation 0·5 g. of chlorine, are dissolved in 50 c.c. of water acidified with sulphuric acid, and titrated with a mixture of 5 g. of bleaching powder and 100 c.c. of water until a drop of the solution ceases to give the ferrous iron reaction when added to a drop of potassium ferricyanide solution. Ferrous ammonium sulphate, which has been strongly recommended by Mohr in place of ferrous sulphate, is quite unsuitable for this test, as a portion of the chlorine is used up in decomposing the ammonia (Biltz).

All methods of bleaching powder analysis must, according to general commercial practice, permit of the determination not only of the chlorine in the solution, but also of that present in the insoluble matter, since the latter too exerts a bleaching action. The insoluble matter must be uniformly distributed through the solution so that the whole forms a uniform thin cream. Hence all methods similar to the above, in which the bleaching powder cream is run in from a burette, are necessarily inaccurate, since the distribution of insoluble matter can never be uniform under such conditions. This source of error is avoided in the following methods.

The sample is prepared for analysis by triturating it with water to a thin cream. The grinding should be extremely intimate, and neither too much nor too little water should be used in the operation. The triturated cream should not contain so little water that the bleaching powder separates out again in lumps while being washed into the litre flask; if this does occur, more water must be added to the cream first prepared, and the whole again triturated for a short time in the mortar. When the operation has been properly performed, the cream will readily mix on shaking with the further water added in the litre flask.

Bunsen's Iodometric method depends on the separation of an amount of iodine equivalent to that of the available chlorine, when a bleach solution and potassium iodide are treated with hydrochloric acid. The iodine liberated remains dissolved in the excess of potassium iodide present, and is titrated with $N/10$ sodium thiosulphate solution (p. 117). If 1 g. of bleaching powder be taken for the titration, the percentage of available chlorine contained in the bleach is found by multiplying the number of the c.c. of thiosulphate required by 0·355. The titration should be performed rapidly to prevent loss of chlorine, and any considerable excess of hydrochloric acid must be avoided. It is best to prepare the cream with 1 g. of bleach and about 100 c.c. of water, and to add to this 2 to 3 g. of potassium iodide and about 10 drops of hydrochloric acid, and to stir once quietly with a glass rod so as to distribute the separated iodine evenly throughout the solution. The thiosulphate is then added rapidly and without stirring until the colour of the solution has been reduced to a faint yellow, starch solution added until the colour becomes deep blue, and the titration continued slowly and drop by drop to completion.

When carefully carried out, the method gives accurate results but great care is necessary, and in no case are the results better than those obtained by Penot's method. The method is consequently but seldom employed in the works, more especially as the consumption of potassium iodide renders it expensive. Wagner's proposal to utilise the decolorised solutions as a solvent for the iodine is not practicable, partly owing to the dilution and partly for other reasons.

A very disturbing effect that frequently occurs in this method, is a rapid reappearance of the blue colour; in the case of impure solutions this often makes it impossible to determine the end-point of the reaction. R. Schultz[1] has found that such cases are of very common occurrence in determining the excess of bleaching powder in disinfected waste liquors, and that the effect is to be ascribed to the presence of oxidising substances such as ferric oxide and calcium chlorate. According to Schultz, very satisfactory results may be obtained, if instead of hydrochloric acid, acetic acid be added to the mixed waste liquor, together with potassium iodide solution and the resulting solution titrated with thiosulphate. In the case of strongly coloured liquors, the end-point is judged by comparing the colour of the titrated solution with that of the original, diluted to an equal bulk.

Bunsen's Distillation method is even less acceptable than the above for technical work. It consists in decomposing the bleaching powder with hydrochloric acid, in a flask, driving off the chlorine by boiling the mixture and passing the evolved gases into a solution of potassium iodide contained in an inverted retort, the liberated iodine being determined by titration. Any chlorate present in the bleach will of course give rise to chlorine by this method. Fogh[2] has devised an apparatus entirely of glass with ground-in parts for the determination.

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[1] *Z. angew. Chem.*, 1903, **16**, 833.

[2] *Cf.* Foerster and Jörre, *J. prakt. Chem.*, 1899, **59**, 58.

It has frequently been shown that the method possesses sources of error,[1] and in no case does the simplicity of the operation compensate for the errors introduced. It is worthy of note that Bunsen[2] himself never once used the distillation method in carrying out his classical work on hypochlorites.

Pontius' Potassium iodide method.[3]—This consists in titrating bleaching powder with potassium iodide solution after previous addition of sodium bicarbonate. 7·09 g. of bleach are dissolved in water in the usual manner and the cream diluted to 1000 c.c.; 50 c.c. of the solution, corresponding to 0·3545 g. of bleaching powder, are measured off, and about 3 g. of solid sodium bicarbonate added to and dissolved in the solution. One to two c.c. of starch solution are then added and the solution immediately titrated (before the liberated hypochlorous acid can react with the starch solution) with *N*/10 potassium iodide solution until the coloration, which is at first reddish brown, and then blue, no longer disappears and the colour becomes a bright and permanent blue. The reaction consists in the formation of potassium iodate from the mixture of hypochlorous acid, sodium bicarbonate, and potassium iodide:—

$$3CaOCl_2\,(=6Cl) + 6NaHCO_3 + KI = KIO_3 + 3CaCO_3 + 6NaCl + 3CO_2 + 3H_2O.$$

This process is also suited to the examination of bleaching solutions, the hypochlorous acid in this case being liberated by addition of boric acid. The method is especially applicable to the approximate determination of substances of quite unknown strength, and Lunge considers it more convenient for this purpose than Penot's method; the latter is, however, more exact in all cases.

Penot's Arsenious acid method.—This method, which finds the greatest acceptance in practice, is, whilst free from all sources of error, both simple and easy of manipulation.[4] The following details for carrying it out are recommended by Lunge.

An alkaline solution of *N*/10 sodium arsenite is employed in place of the acid solution used in the Gay-Lussac method. The preparation of this solution has been described on p. 122. In alkaline solution the oxidation of arsenious to arsenic acid, which requires 4 atoms of chlorine, per gram molecule, takes place smoothly and without loss of chlorine, the end-point of the titration being shown with extreme sharpness by the blue coloration produced on iodised starch paper. An excess of the arsenite solution may be added, if preferred, and such excess titrated back with *N*/10 iodine solution. This latter method is, however, seldom employed, since it necessitates the use of two standard solutions and is in no way more accurate.

In carrying out the test, 7·09 g. of the thoroughly mixed bleach

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[1] *Cf.* Winkler, *Z. angew. Chem.*, 1903, **16**, 33.

[2] *Annalen*, 1856, **86**, 265.

[3] *Chem. Zeit.*, 1904, **28**, 54.

[4] *J. prakt. Chem.*, 1896, **54**, 59.

samples are ground in a porcelain mortar with a little water to a uniform thin cream, diluted by addition of more water, and the whole washed into a litre flask and made up to 1000 c.c. The lip of the mortar should be greased on its under side with a little fat or vaseline, to facilitate the transference of the liquid from the mortar to the flask. Fifty c.c. of the thoroughly mixed solution (=0·3545 g. bleaching powder) are pipetted off and transferred to a beaker, where they are thoroughly stirred, whilst the $N/10$ arsenite solution is run in until nearly the full quantity expected to be required has been added. A drop of the solution is then placed on filter paper which has been moistened with a little potassium iodide starch solution. According to the depth of the blue colour obtained (in presence of larger quantities of chlorine a brown stain is produced), more or less additional arsenite solution is added and the spotting repeated until the test paper remains white, or until only a quite inappreciable coloration is produced. Each 1 c.c. of the arsenite required represents 1 per cent. of available chlorine in the sample.

Suitable iodised starch paper for this test is prepared as follows :—One g. of starch is boiled with 100 c.c. of water, the solution filtered and 0·1 g. of potassium iodide added to the filtrate. The filter paper is then soaked in this solution and dried on a porcelain or similar plate at 40° to 50°. For the spotting test the paper should be moistened, as the reaction is much cleaner and more delicate with moist than with dry paper. Three or four pieces of the paper are spread on a glass plate and any excess of water allowed to flow off; they are then ready for spotting. The disappearance of the blue colour may be very sharply determined if the glass plate is examined by transmitted light towards the end of the titration.

Lunge's Gas-volumetric method.—Penot's method is so simple, convenient, and accurate, that no other method is really needed. It is, however, desirable to have an independent method, which may, when required, be used as a check. Lunge's gas-volumetric method serves this purpose. The hypochlorite is decomposed with hydrogen peroxide in a nitrometer or gas volumeter, and the volume of the oxygen liberated measured. The reaction takes place according to the following equation :—

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

That is, the volume of active chlorine present is exactly equal to the volume of the oxygen liberated.[1] The operation is carried out in a nitrometer provided with a decomposition bottle, as in the analysis of manganese ore (*cf.* pp. 137 and 479). The addition of acid, as recommended by Vanino, is of doubtful value.[2]

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[1] *Cf.* Lunge, *Chem. Ind.*, 1885, **8**, 168; *Ber.*, 1886, **19**, 868; *Z. angew. Chem.*, 1890, **3**, 8; Baumann and Vanino, *Z. angew. Chem.*, 1890, **3**, 80, 186, 509.

[2] Cf. *Z. angew. Chem.*, 1890, **3**, 136.

The bleaching powder solution is advantageously prepared so that 25 c.c., the volume taken for the reaction, contain 1 g. of bleaching powder. This will be the case if 20 g. of the bleach are triturated with water as described above, and the resultant cream diluted with water to 500 c.c.; working with 25 c.c. of such a solution, each 1 c.c. of oxygen evolved, reduced to 0° and 760 mm., equals 0·3166 per cent. of chlorine. The test should be carried out with a bulb nitrometer graduated to 140 c.c. Should it be desired to work with a smaller nitrometer, say of 30 to 50 c.c. capacity, only 5 c.c. of the above solution should be taken, in which case each 1 c.c. of oxygen evolved will correspond to $5 \times 0{\cdot}3166 = 1{\cdot}583$ per cent. of chlorine. A still more convenient plan is to dissolve 7·915 g. of bleach in 250 c.c. of water, and to take 10 c.c. of the milky solution for the test; the percentage of available chlorine is then equal to the number of c.c. of oxygen liberated. A 50 c.c. instrument can be used under these conditions.

The hydrogen peroxide is introduced into the inner compartment of the decomposition bottle, and rendered just alkaline by the addition of a few drops of sodium hydroxide solution to prevent the evolution of carbon dioxide; the bleaching powder solution is then placed in the outer compartment. The shaking should only be continued for from one to two minutes after mixing the solutions, and the volume of gas evolved should be read off immediately and before any spontaneous evolution of oxygen occurs. The addition of a considerable excess of sodium hydroxide to the peroxide must be avoided, but it is safe to add the hydroxide until the solution is distinctly alkaline and a flocculent precipitate appears. This addition should, of course, be made to each portion of peroxide immediately before the test. The hydrogen peroxide solution should not be too concentrated; 1 c.c. treated with excess of bleaching powder solution in the nitrometer should not give more than 7 c.c. total oxygen. If it is too strong, a little water may be added directly to the solution in the decomposing flask. A small excess of water is immaterial, and it also makes no difference whether the hydrogen peroxide is employed in considerable or only in small excess.

Baumann[1] has shown that in carrying out the gas-volumetric method with hydrogen peroxide it is very easy to obtain too high a result when the hydrogen peroxide solution has been kept in a stoppered bottle and has not been shaken before use; under these circumstances the thorough shaking necessary in the analysis may give rise to the liberation of appreciable quantities of oxygen (from 0·5 to 2 mg. oxygen from 10 c.c. of hydrogen peroxide). This oxygen results from the continuous, gradual decomposition of the peroxide and remains dissolved in the peroxide solution, owing to the somewhat higher pressure exerted in the stoppered bottle.

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[1] *Z. angew. Chem.*, 1891, 4, 450.

The fear that the solid particles present in the milky bleach solution might exert a catalytic influence and thereby lead to high results, has proved to be groundless. The oxygen can be collected over either mercury or water.

According to Lunge, the gas-volumetric method of estimating bleach always gives higher results than are obtained by Penot's method. As the result of a very extended series of tests, he states that such excess of available chlorine amounts on the average to 0·15, or at most 0·2 per cent. The cause of this difference has not yet been definitely elucidated.

Vanino's Hydrogen peroxide method.[1] — This is a volumetric method for the analysis of bleaching powder based on the above reaction.

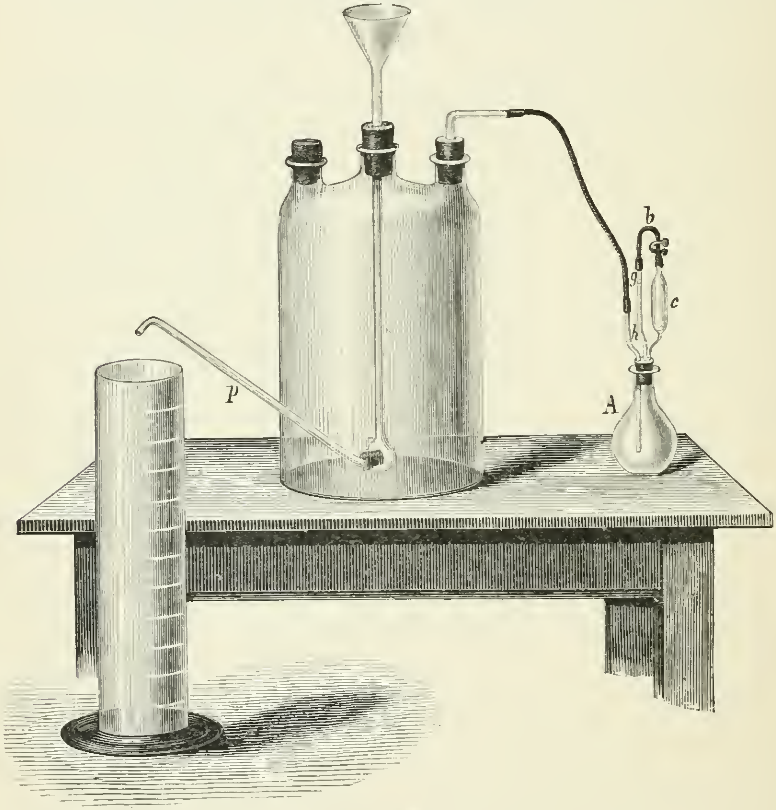

FIG. 144.

The bleaching powder is decomposed by adding an excess of hydrogen peroxide, standardised by means of permanganate, and the undecomposed peroxide is titrated back. The method is more complicated than that of Penot, and offers no special advantages.

[1] *Z. angew. Chem.*, 1890, 3, 83.

Vanino[1] recommends the following apparatus (Fig. 144) for the rapid approximate determination of available chlorine. It is very convenient, and is adapted for use by workmen in bleaching works, etc. It is also generally suitable for other tests in which an evolved gas is measured when rapid approximate results are wanted.

The bleaching powder is weighed off on a hand balance, rubbed to a cream with water, and introduced into the generating flask A; the solution of hydrogen peroxide is placed in *c*. The outlet tube, *p*, of the gas-holder is best drawn out to a point, to reduce the tendency to form air-bubbles. The gas-holder is filled with water, and before each test the tube *p* is lowered so as to allow a few drops of water to escape; this tube must remain filled with water, both at the beginning and at the end of each experiment. A measuring cylinder is placed under the outlet of the tube *p*. By opening the pinchcock at *b*, the hydrogen peroxide solution flows into the bleach solution and the oxygen evolved displaces its own volume of water, which is collected in the measuring cylinder. A certain time is allowed to elapse after each test before the volume of water in the cylinder is read off. The results are calculated from Vanino's table (p. 508), the figures in which are for the moist gas.

Weight of 1 c.c. Chlorine in milligrams (*Vanino*),

for barometric pressures from 700 to 770 mm. and for temperatures from 10° to 25° C.:—

$$\left[\text{Value of } \frac{(b-w)3.16696}{760(1+0.00366t)}\right]$$[2]

A deduction of 1 mm. must be made from the barometric reading at temperatures from 10° to 12°, of 2 mm. at 13° to 14°, and of 3 mm. at 20° to 25°, so as to reduce the reading of the barometer to 0°.

If, for example, 1·10 g. of bleaching powder are taken for the test and the volume of water collected, corresponding to the oxygen evolved, measures 140 c.c. at 10° and 720 mm. pressure, the calculation is made as follows. From the table the factor corresponding to 10° and 720 mm. is 2·858; this multiplied by 0·140 the volume, expressed in litres, of the water collected gives 0·400 as the weight in g. of the chlorine contained in the 1·10 g. of bleaching powder, which, therefore, tests 36·36 per cent.

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[1] *Z. angew. Chem.*, 1890, **3**, 509.

[2] This table is based on the value 3.16696 g. as representing the weight of 1 litre of chlorine, whereas the correct figure according to the most recent determinations is 3·219. Consequently, the whole of the values given in Vanino's table are 1·6 per cent. too low. Vanino has more recently (*Z. anal. Chem.*, 1902, **41**, 539), extended the table to 30° and for the odd values for the barometric pressure, within the above limits.

Barometric Pressure Mm.	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	Barometric Pressure. Mm.
700	2·777	2·765	2·752	2·740	2·728	2·715	2·702	2·690	2·677	2·664	2·651	2·637	2·624	2·610	2·597	2·583	700
702	2·785	2·773	2·761	2·748	2·736	2·723	2·710	2·698	2·684	2·671	2·658	2·645	2·632	2·618	2·604	2·590	702
704	2·793	2·781	2·769	2·756	2·744	2·731	2·718	2·705	2·692	2·679	2·666	2·653	2·639	2·626	2·612	2·598	704
706	2·801	2·789	2·777	2·764	2·752	2·739	2·726	2·713	2·700	2·687	2·674	2·660	2·647	2·633	2·619	2·606	706
708	2·809	2·797	2·785	2·772	2·760	2·747	2·734	2·721	2·708	2·695	2·682	2·668	2·655	2·641	2·627	2·613	708
710	2·817	2·805	2·793	2·780	2·767	2·755	2·742	2·729	2·716	2·702	2·689	2·676	2·663	2·649	2·635	2·621	710
712	2·826	2·813	2·801	2·788	2·775	2·763	2·750	2·737	2·724	2·710	2·697	2·684	2·670	2·656	2·643	2·629	712
714	2·834	2·821	2·808	2·796	2·783	2·770	2·758	2·745	2·732	2·718	2·705	2·691	2·678	2·664	2·650	2·636	714
716	2·842	2·829	2·816	2·804	2·791	2·778	2·765	2·753	2·739	2·726	2·713	2·699	2·686	2·672	2·658	2·644	716
718	2·850	2·837	2·824	2·812	2·799	2·786	2·773	2·760	2·747	2·734	2·720	2·707	2·693	2·679	2·665	2·651	718
720	2·858	2·845	2·832	2·820	2·807	2·794	2·781	2·768	2·755	2·741	2·728	2·715	2·701	2·687	2·673	2·659	720
722	2·866	2·853	2·840	2·828	2·815	2·802	2·789	2·776	2·763	2·749	2·736	2·723	2·709	2·695	2·681	2·667	722
724	2·874	2·861	2·848	2·836	2·823	2·810	2·797	2·784	2·771	2·757	2·744	2·730	2·716	2·703	2·689	2·674	724
726	2·882	2·869	2·856	2·844	2·831	2·818	2·805	2·792	2·779	2·765	2·751	2·738	2·724	2·710	2·696	2·682	726
728	2·890	2·877	2·864	2·852	2·839	2·826	2·813	2·799	2·786	2·773	2·759	2·746	2·732	2·718	2·704	2·690	728
730	2·898	2·885	2·872	2·860	2·847	2·834	2·821	2·807	2·794	2·780	2·767	2·754	2·740	2·726	2·712	2·697	730
732	2·906	2·893	2·880	2·868	2·854	2·841	2·828	2·815	2·802	2·788	2·775	2·761	2·747	2·733	2·719	2·705	732
734	2·914	2·901	2·888	2·876	2·862	2·849	2·836	2·823	2·809	2·796	2·782	2·769	2·755	2·741	2·727	2·712	734
736	2·922	2·909	2·896	2·883	2·870	2·857	2·844	2·831	2·817	2·804	2·790	2·777	2·763	2·749	2·734	2·720	736
738	2·930	2·917	2·904	2·891	2·878	2·865	2·852	2·839	2·825	2·812	2·798	2·784	2·770	2·756	2·742	2·728	738
740	2·938	2·925	2·912	2·899	2·886	2·873	2·860	2·847	2·833	2·819	2·806	2·792	2·778	2·764	2·750	2·735	740
742	2·946	2·933	2·920	2·907	2·894	2·881	2·868	2·855	2·841	2·827	2·814	2·800	2·786	2·772	2·758	2·743	742
744	2·954	2·941	2·928	2·915	2·902	2·889	2·876	2·862	2·849	2·835	2·821	2·808	2·794	2·780	2·765	2·751	744
746	2·962	2·949	2·936	2·923	2·910	2·897	2·884	2·870	2·857	2·843	2·829	2·815	2·801	2·787	2·773	2·758	746
748	2·970	2·957	2·944	2·931	2·918	2·905	2·891	2·878	2·864	2·851	2·837	2·823	2·809	2·795	2·780	2·766	748
750	2·978	2·965	2·952	2·939	2·926	2·913	2·899	2·886	2·872	2·858	2·845	2·831	2·817	2·802	2·788	2·774	750
752	2·986	2·973	2·960	2·947	2·934	2·921	2·907	2·894	2·880	2·866	2·852	2·838	2·824	2·810	2·796	2·781	752
754	2·994	2·981	2·968	2·955	2·942	2·929	2·915	2·901	2·888	2·874	2·860	2·846	2·832	2·818	2·804	2·789	754
756	3·002	2·989	2·976	2·963	2·950	2·936	2·923	2·909	2·896	2·882	2·868	2·854	2·840	2·825	2·811	2·796	756
758	3·010	2·997	2·984	2·971	2·957	2·944	2·931	2·917	2·904	2·890	2·876	2·862	2·848	2·833	2·819	2·804	758
760	3·018	3·005	2·992	2·979	2·965	2·952	2·939	2·925	2·911	2·897	2·884	2·869	2·855	2·841	2·827	2·812	760
762	3·026	3·013	3·000	2·987	2·973	2·960	2·947	2·933	2·919	2·905	2·891	2·877	2·863	2·849	2·834	2·819	762
764	3·035	3·021	3·008	2·995	2·981	2·968	2·954	2·941	2·927	2·913	2·899	2·885	2·871	2·856	2·842	2·827	764
766	3·043	3·029	3·016	3·003	2·989	2·976	2·962	2·949	2·935	2·921	2·907	2·893	2·878	2·864	2·849	2·835	766
768	3·051	3·037	3·024	3·011	2·997	2·984	2·970	2·957	2·943	2·929	2·914	2·900	2·886	2·872	2·857	2·842	768
770	3·059	3·045	3·033	3·019	3·005	2·991	2·978	2·965	2·951	2·937	2·922	2·908	2·894	2·879	2·865	2·850	770

Robert and Roncali[1] determine hypochlorites by measuring the nitrogen evolved by decomposition with hydrazine sulphate.

The carbon dioxide present in bleaching powder is occasionally determined. This may be done by decomposing the bleach with hydrochloric acid and passing the liberated chlorine and carbon dioxide into an ammoniacal solution of calcium chloride (one part $CaCl_2.6H_2O$, six parts water, and ten parts aqueous ammonia, sp. gr. 0·96, mixed and allowed to stand for some time in a similar manner to that described on p. 430 for liberating the sulphuretted hydrogen from sulphides). The chlorine reacts with the ammonia according to the equation:—

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

The reaction may be hastened by boiling the solution. The carbon dioxide is converted into calcium carbonate, which is filtered off and estimated in the usual manner.

The method devised by Lunge and Rittener (p. 514) is both more convenient and more accurate.

II. Bleaching Solutions and Electrolytic Liquors

Bleaching solutions consist essentially of mixtures of hypochlorites and chlorides, and in many cases also contain free hypochlorous acid. The base may be calcium, potassium, sodium (in Eau de Javel and "chloros"), or magnesium, zinc, etc. Whether such solutions be prepared by the double decomposition of bleaching powder with various salts, or by passing chlorine into milk of lime, sodium carbonate, etc., or by the electrolysis of chloride solutions, the constituents are hypochlorite, chloride, free hypochlorous acid, and chlorate, with bases such as the alkalis or calcium; the solutions may also contain carbonate in addition to caustic alkali.

The same constituents are present in the liquors which result from the electrolytic manufacture of caustic alkali or of chlorate, but in this case the ratio between the various substances is very different from that existing in bleaching solutions. The same methods of analysis are, however, applicable in both instances.

James and Richey[2] have given a useful summary of the various methods of analysis adopted in electrolytic works.

Available Chlorine.—In the case of bleach solutions the determination of the available chlorine is in most instances sufficient; this is carried out as described under bleaching powder, p. 499. Such available chlorine may be due either to hypochlorites or to the free hypochlorous acid. Since the bleaching value is very different according to whether the hypochlorous acid is free or combined, a point on which the exceptionally great bleaching value of many liquors, especially electrolytic

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[1] *Chem. Centr.*, 1904. I., 1294.

[2] *J. Amer. Chem. Soc.*, 1902, **24**, 469.

liquors, depends, it may be necessary to determine the quantity of free hypochlorous acid accompanying the hypochlorite salts, in solution. Insoluble substances or material remaining undissolved, such as zinc oxide, calcium hydroxide, etc., may be taken to be without action on hypochlorous acid. Thus (should the liquor be found to contain free base in solution) free hypochlorous acid may be regarded as absent ; the latter will only occur when all the basic material present has been saturated by acid radicals, such as hypochlorous acid, chloric acid, hydrochloric acid, carbonic acid, sulphuric acid, etc. The various salts will, of course, be more or less hydrolytically or electrolytically dissociated according to the degree of concentration of the solution, but such dissociation is without influence from the analytical standpoint.

Free Hypochlorous acid.—From the above considerations conclusions can be drawn regarding the presence of free hypochlorous acid by examining the solution, after filtering off from insoluble basic substances, in the first place for total bases, and in the second place for chlorine present as chloride (cf. *infra*), carbonic acid, sulphuric acid, and if necessary for such other acids as may be present, and further for "available chlorine," that is, for chlorine present as hypochlorite. If calculation should show that the quantity of base, the Na_2O, for instance, in the case of a soda solution, is insufficient to neutralise the whole of the acids found to form sodium chloride, sulphate, carbonate, and hypochlorite, it may be concluded that free hypochlorous acid is present.

A much simpler method depends upon the fact that when a salt of hypochlorous acid reacts with potassium iodide, two molecules of the base are liberated, whilst in the case of free hypochlorous acid, only one molecule of the base is set free :—

$$NaOCl + 2KI + H_2O = NaCl + 2KOH + I_2.$$
$$HOCl + 2KI = KCl + KOH + I_2.$$

Consequently, if the liberated iodine be removed by titrating the solution with thiosulphate, the two products can then be distinguished by titrating with standard acid. Any alkali carbonate present in the original solution must, of course, be allowed for (*cf.* p. 516).

The separation of free hypochlorous acid by distillation, with or without the addition of other acids, is too uncertain to be of value.

Lunge[1] has described a simple method for distinguishing between free chlorine and hypochlorous acid, based on their reaction with a neutral solution of potassium iodide ; hypochlorous acid forms an alkali hydroxide, whilst in the case of chlorine the solution remains neutral, as shown in the following equations :—

$$1.\ ClOH + 2KI = KCl + KOH + I_2.$$
$$2.\ Cl_2 + 2KI = 2KCl + I_2.$$

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[1] *Chem. Ind.*, 1881, 4, 293.

In the first case the liberated iodine reacts with the potassium hydroxide to produce various compounds, especially potassium iodate; this may, however, be prevented by adding, at the start, the requisite quantity of hydrochloric acid to convert the free alkali into potassium chloride. If the quantity of acid added be known, it is then only necessary to titrate with standard alkali. The reactions in acid solution are:—

$$1a.\ ClOH + 2KI + HCl = 2KCl + I_2 + H_2O.$$
$$2a.\ Cl_2 + 2KI + HCl = 2KCl + I_2 + HCl.$$

That is, in the case of hypochlorous acid one molecule of hydrochloric acid is neutralised for each molecule of hypochlorous acid reacting with potassium iodide, whilst in the case of chlorine the hydrochloric acid added remains unchanged. If then, the solution be first titrated with $N/10$ thiosulphate solution, and then with $N/10$ sodium hydroxide solution, in 1*a* the volume of thiosulphate solution used will be equal to twice the difference between the number of c.c. of $N/10$ alkali necessary to neutralise the full quantity of acid originally added and that now required to neutralise the excess of free acid. In 2*a*, no such difference will occur. For intermediate cases it is easy to calculate the ratio between the hypochlorous acid and chlorine, since for each 1 c.c. $N/10$ hydrochloric acid neutralised, 2 c.c. $N/10$ thiosulphate must be allotted to hypochlorite.

This method is difficult of application in the presence of free alkali or alkaline carbonate, but in such cases free chlorine is hardly likely to be present.

Chlorates may be estimated by first determining the available chlorine according to one or other of the methods described on p. 500, and then determining this and chlorate-chlorine together, by boiling with ferrous sulphate and titrating back the excess of the latter with permanganate, as described on p. 497. The difference between the two figures so obtained gives the chlorine present as chlorate. The chlorine present as hypochlorite and chlorate may also be determined iodometrically, by boiling with strong hydrochloric acid and collecting the evolved gas in potassium iodide solution (*cf.* p. 502).

According to Winteler,[1] the latter method is very inexact, but results accurate to within 0·1 to 0·2 per cent. are obtainable by the ferrous sulphate method, provided the solution containing the hypochlorite and chlorate be added to the measured excess of ferrous sulphate solution and the mixture be allowed to stand for several minutes before heating, air of course being excluded.

The direct method due to Fresenius[2] is preferable to the above, but it is somewhat more troublesome. The solution to be tested is treated with an excess of neutral lead acetate solution; a precipitate is formed

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[1] *Z. angew. Chem.*, 1903, **16**, 33.

[2] *Ibid.*, 1895, **8**, 501.

which gradually turns brown with liberation of chlorine, and which contains a quantity of lead peroxide corresponding to the hypochlorite present :—

$$Ca(OCl)_2 + PbCl_2 = PbO_2 + CaCl_2 + Cl_2.$$

The solution is allowed to stand for eight to ten hours, with frequent agitation, until all smell of chlorine has disappeared. The chlorine liberated reacts with the lead acetate solution to form lead chloride, lead peroxide, and free acetic acid. The precipitate, consisting of the peroxide and chloride of lead, is filtered off and washed, the filtrate and washings concentrated by evaporation, and the contained lead and calcium precipitated by addition of sodium carbonate in slight excess ; the filtrate, which then contains the chlorate as the sodium salt, is evaporated and its chlorate content determined (p 497.).

For liquors which contain a large amount of hypochlorite together with chlorate, as is the case with electrolytic and other bleaching solutions, Ditz and Knöpflmacher[1] recommended estimating the chlorate iodometrically by decomposition at the ordinary temperature with strong hydrochloric acid and potassium bromide. The process has recently been modified by Ditz[2] as follows ; the method is also suitable for the examination of chlorate liquors. The apparatus employed is shown in Fig. 145. The bottle *a* has a capacity of about 1500 c.c., and may be closed either by the stopper *b*, or by the headpiece *c*, as shown in the figure. The latter is provided with a dropping funnel, *d*, and with an absorption tube, *c*.

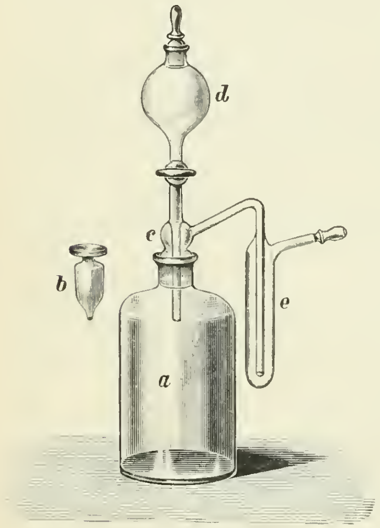

Fig. 145.

The volume of chlorate solution used for a determination should be such as to contain approximately 0·1 g. of chlorate, calculated as $KClO_3$. Should it be necessary to estimate the chlorate in a mixture containing both chlorate and hypochlorite, the volume taken for analysis should be so regulated that the total consumption of $N/10$ sodium thiosulphate solution will be between 40 to 50 c.c. The measured volume of chlorate liquor, together with 10 c.c. of a 10 per cent. potassium bromide solution, are introduced into the bottle, and after the absorption tube has been filled to two-thirds of its height with a 5 per cent. solution of potassium iodide, concentrated hydrochloric acid is added from the dropping funnel *d*. If the volume

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[1] *Z. angew. Chem.*, 1899, **12**, 1195.

[2] *Chem. Zeit.*, 1901, **25**, 727.

of the chlorate solution does not exceed 25 c.c., 50 c.c. of acid are added, and proportionately more if more than 25 c.c. are required for the analysis. The liberated bromine is absorbed by the potassium iodide in *e*; to prevent the solution being sucked back into *a*, the stopper on the exit-tube of *e* is inserted. After the whole has been allowed to stand for five minutes, from 500 to 600 c.c. of distilled water are introduced through the dropping funnel, followed at a moderate rate by about 20 c.c. of the 5 per cent. potassium iodide solution. If more than 50 c.c. of hydrochloric acid have been used for the decomposition, proportionately more water must be added. The mixture is well agitated, the contents of the absorption tube blown over into *a*, the tube together with the headpiece thoroughly washed, the latter replaced by the glass stopper, and the liberated iodine determined by titration with *N*/10 thiosulphate solution. If 1 c.c. of the thiosulphate solution equals *a* g. iodine and the volume required for the titration of the separated iodine be *b* c.c., the weight of chlorate present is given by the equation :—

$$g\ \mathrm{KClO_3} = a \times b \times \frac{122.60}{761.8} = 0.1609\ a \times b,$$

and the quantity of potassium chloride equivalent to this by the equation :—

$$g\ \mathrm{KCl} = a \times b \times \frac{74.60}{761.8} = 0.0979\ a \times b.$$

When examining mixtures containing both hypochlorite and chlorate, the quantity of hypochlorite present must be previously determined and allowed for.

Kolb and Davidson[1] also carry out the determination at the ordinary temperature. They dissolve about 0·08 g. of the chlorate in 10 c.c. of water, free from air, in a 500 c.c. flask, heat the solution on the water-bath, and allow it to cool in a current of carbon dioxide; 2 g. of potassium iodide and 50 c.c. of air-free hydrochloric acid of sp. gr. 1·12 are then added, the whole allowed to stand for an hour, protected from the light, diluted with boiled water saturated with carbon dioxide to 300 c.c., and the liberated iodine finally titrated with sodium thiosulphate.

M. Scholtz[2] reduces the chlorate to chloride with nitric acid and sodium nitrite, adds a measured volume of *N*/10 silver nitrate solution, and titrates back the excess with ammonium thiocyanate, using ferric ammonium alum as indicator.

Hendrixon[3] reduces the chlorate with metallic iron, and titrates the resulting chloride, after oxidising the iron with nitric acid.

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[1] *Z. angew. Chem.*, 1904, **17**, 1883; 1905, **18**, 1047, 1693. *Cf.* also, Ditz, *ibid.*, 1905, **18**, 1518.

[2] *Arch. Pharm.*, 1905, **243**, 353; *J. Soc. Chem. Ind.*, 1905, **24**, 904.

[3] *Amer. Chem. J.*, 1904, **32**, 242.

Chloride-chlorine.—The chlorine present as chloride is most conveniently estimated in the following manner. The available chlorine is first determined by Penot's method (p. 503), whereby it is completely converted to chloride, whilst the arsenite is oxidised to sodium arsenate. The latter compound is an exceptionally good indicator for the silver nitrate titration ; in fact, it is so much superior to potassium chromate that it is unnecessary to make any deduction for the excess of silver nitrate necessary to produce the coloration. It is therefore only necessary to nearly neutralise the free alkali by cautious addition of nitric acid (a slight excess of alkali is not harmful, excess of free acid is) and then to titrate with silver nitrate solution, with good agitation, as described on p. 123, until the precipitate becomes red owing to the formation of a small quantity of silver arsenate. If preferred, the chloride may, of course, be determined gravimetrically. On deducting the chlorine corresponding to the hypochlorite found, from the total chlorine as determined above, the quantity of chlorine present as chloride in the original solution is obtained.

Carbonic acid.—In estimating carbonic acid, the details given in describing the analysis of Deacon gases (p. 491) and of bleaching powder (p. 509) apply. Naturally, appreciable quantities of carbonic acid cannot exist in bleach solutions containing calcium oxide or magnesia ; they may, however, be present in potash or soda bleaching solutions and in electrolytic potash and soda liquors. This carbonic acid may be estimated by first converting the hypochlorite to chloride by boiling with ammonia solution free from carbonate, allowing the boiled solution to cool under exclusion of carbon dioxide, and then determining the total alkalinity by titrating a portion of the solution with methyl orange as indicator. The alkali hydroxide is estimated in a second portion of the solution after addition of barium chloride, as described on pp. 72 and 424. The difference between the two titrations gives the amount of carbonate present. The carbonic acid may also be determined directly, after decomposing the hypochlorite in the manner described above, by liberating it with a strong acid and estimating it either gravimetrically or gas-volumetrically (p. 149). Blattner's method (cf. *infra*) can also be used.

The estimation of carbon dioxide in presence of chlorine can also be carried out by the simplified Lunge-Marchlewski method devised by Lunge and Rittener[1] (*cf.* p. 153).

The apparatus employed is shown in Fig. 146. The decomposition flask B has a capacity of about 30 c.c. ; it is fitted with a tap-funnel C and capillary exit-tube D, which is cut off flush with the bottom of the rubber stopper in B. D is connected with the exit-tube of the Bunté burette A, as shown ; the ungraduated portion of the burette must be calibrated.

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[1] *Z. angew. Chem.*, 1906, 19, 1849.

To carry out a determination, sufficient substance or solution is introduced into B to evolve not more than 60 c.c. of gas; D is then connected with the burette, the taps E and F opened, and the whole evacuated by attaching an ordinary pump to F. This tap is then closed and connected with the pressure-bottle G, charged with a saturated brine solution, which is used as the confining liquid in place of mercury. A little of the brine solution is allowed to enter the capillary portion of the bottom of the nitrometer, as a check on any possible leakage, and the tap F again closed.

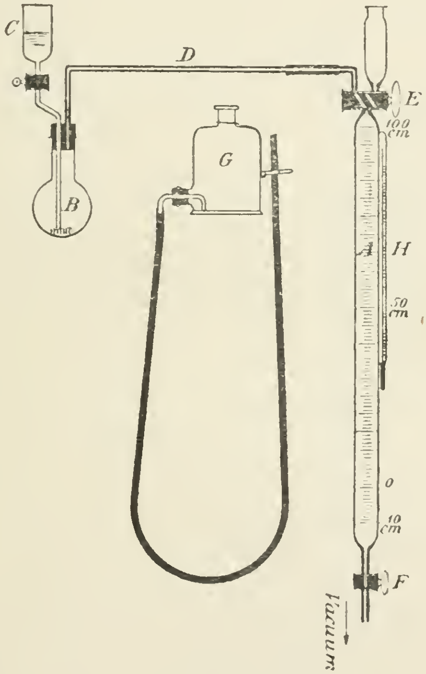

Fig. 146.

The substance in B is then decomposed by adding hydrochloric acid, drop by drop, from the tap-funnel C; when the evolution of gas slackens the contents of B are heated, and the complete evolution of the liberated gases facilitated by the addition of from 2 to 3 c.c. of hydrogen peroxide; on again heating, the evolved oxygen drives out all the dissolved gas. The burette is then disconnected, allowed to stand for about twenty minutes and the volume of gas read, after adjusting the pressure by means of the bottle G. After taking the reading, a measured excess of an *N*/10 sodium arsenite solution is added, through the burette funnel, to absorb the chlorine, and any portion adhering to the funnel washed in with a little water; this solution floats on the heavier solution of brine. The pressure-bottle G is then detached and the carbon dioxide absorbed by sodium hydroxide solution introduced through E; as all the chlorine has been previously removed, no chlorate can be formed during this absorption. When the absorption is complete the residual volume of gas is read, which, deducted from the original reading, gives the volume of carbon dioxide and chlorine, after correcting each reading for temperature and pressure; the vapour pressure of the brine solution may be taken as 80 per cent. of that of pure water.

To determine the chlorine, the contents of the burette are washed out into a beaker, acidulated with hydrochloric acid, an excess of sodium bicarbonate added, and the unchanged arsenite titrated with $N/10$ iodine solution. The volume of carbon dioxide collected is then calculated by difference.

Bases.—As regards the bases, should only one be present, as is usually the case, the total quantity may be estimated by conversion to sulphate by evaporating with sulphuric acid. Calcium and magnesium may also be determined as oxalate and pyrophosphate respectively, after first decomposing the hypochlorite by boiling with a strong acid.

Alkali hydroxide and carbonate.—Blattner[1] describes the following neat method for determining these constituents in Eau de Javel. It depends upon the fact that phenolphthalein preserves its red colour in hypochlorite solution so long as alkali hydroxide is present, but that the colour is destroyed by free chlorine as soon as all the hydroxide has been removed, and does not return on the further addition of free alkali. Ten c.c. of the bleach liquor are diluted with 150 c.c. of previously boiled and distilled water, a few drops of a 1 per cent. alcoholic solution of phenolphthalein added, and the solution then titrated with normal acid, continuous agitation being maintained during the addition of the acid. The whole of the alkali hydroxide is neutralised when the coloration produced by the addition of a fresh drop of phenolphthalein solution disappears on shaking the solution for five seconds. Each 1 c.c. of normal acid used corresponds to 0·03105 g. Na_2O or 0·04006 g. NaOH. The total alkalinity, $NaOH + Na_2CO_3$, is determined in a second portion of the liquor by boiling with ammonia until the hypochlorite has been decomposed and all unchanged ammonia driven off, and then titrating with acid in the usual manner. The above methods are especially suitable for the examination of caustic potash or caustic soda solutions produced electrolytically, which usually contain hypochlorite.

The following is a very simple method of determining the free alkali. A small quantity of chemically pure, neutral hydrogen peroxide

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[1] Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 439.

is added to the solution to decompose the hypochlorite, according to the equation $NaOCl+H_2O_2=NaCl+O_2+H_2O$, and the sodium hydroxide and carbonate present are then titrated in the usual manner (*cf.* pp. 72 and 424).

H. v. Huber[1] has described a method for the examination of electrolytic liquors which contain chromate. Phenolphthalein is, in this case, unsuitable as an indicator for the free alkali present; methyl orange, however, gives a perfectly sharp colour change at the point where potassium chromate is converted into the bichromate. If, therefore, the chromate content is known, it is only necessary to deduct from the total acid required for titration the quantity necessary to convert the chromate into bichromate. If the quantity of chromate present is not known, the chromate is precipitated by addition of barium chloride, and the solution then titrated with acid. Where the quantity of chromate present is small, it is not necessary to filter the solution before titrating. Any hypochlorite or free hypochlorous acid in the liquor must first be removed; this may be done without affecting the alkalinity, by addition of neutral sodium sulphite or of sodium thiosulphate. If sodium sulphite be used, an excess must be avoided, since with methyl orange the colour change only occurs when such excess has been converted to the acid sulphite which involves the consumption of the corresponding quantity of acid (*cf.* p. 65).

III. POTASSIUM CHLORATE

The potassium chlorate of commerce is generally almost chemically pure, and contains only a very small trace of chloride, the quantity of which should not exceed 0·05 per cent. For this reason it is necessary to take a somewhat large quantity of chlorate, say 50 g., for the determination of the *chloride.* The chlorate is dissolved in distilled water, and the chloride precipitated by addition of silver nitrate solution. The distilled water employed must be perfectly free from chlorides. The chlorate should dissolve without residue, and the solution should not be coloured by organic matter. Ammonium sulphide should not produce any coloration, indicating the absence of iron, manganese, or lead. Garnier[2] found arsenic in potassium chlorate.

Potassium nitrate only occurs in potassium chlorate as an adulterant. According to the German Pharmacopœia, its presence is detected by fusing the chlorate and examining the melt for alkalinity; authorities are, however, agreed that this method is misleading, since even pure potassium chlorate gives an alkaline reaction after fusion. The following reactions are more satisfactory.[3]

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[1] *Zeit. Electrochem.*, 1901, 7, 396.

[2] *Fischer's Jahresber.*, 1885, p. 260.

[3] Krauch, *The Testing of Chemical Reagents for Purity*, p. 227.

One g. of the salt is heated with 5 c.c. of sodium hydroxide solution; should ammonia be evolved, indicating the presence of ammonium salts, the solution is boiled until all ammonia has been expelled. The solution is then cooled, 0·5 g. of zinc filings and iron powder added, and the whole again heated. Any ammonia then liberated is due to the presence of nitrate. According to Scholvien,[1] the potassium chlorate is heated until the residual potassium chloride has also been brought to fusion. The melt is dissolved in water, and the solution treated with dilute sulphuric acid followed by zinc iodide-starch solution. The coloration produced should not be sufficient to render the solution opaque. A faint blue coloration is permissible, since with 0·01 per cent. of nitrate the colour produced is so intense that the solution is quite opaque.

A quantitative determination of the chloric acid in commercial chlorate is scarcely ever undertaken, owing to the small amount of impurity present; it may, however, be carried out as described on p. 497. This determination would be necessary for the indirect estimation of sodium and potassium chlorate in a mixture of the two salts; so far, such mixtures do not, however, appear to occur in practice.

IV. LIQUID CHLORINE

The following physical properties of liquid chlorine are given by A. Lange.[2]

Specific gravity at 0°, 1·469; 15°, 1·426; 30°, 1·381.
Vapour pressure at 0°, 3·7; 15°, 5·8; 30°, 8·7 atmos.

One kilo corresponds to a volume of 316 litres measured at 0° and 760 mm. pressure.

Critical temperature, 146°.
Critical pressure, 93·5 atmos.
Boiling-point at 760 mm., − 33°·6.
Melting-point of the solidified gas, − 102°.

Conditions of carriage on the German railways:—The capacity of the containing vessel must be at the rate of 0·9 litre for each 1 kilo of chlorine; the cylinders must be officially tested up to a pressure of 50 atmospheres; the pressure test must be repeated annually.

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[1] *Apoth. Zeit.*, 1887, 408.

[2] *Taschenbuch. d. Berliner Bezirksvereines Deutscher Chemiker*, 1898-99, p. 82.

Pressure and Specific Gravity of Liquid Chlorine.

R. Knietsch.[1]

Temperature. Degrees.	Pressure.	Specific Gravity.	Mean Coefficient of Expansion.
- 88	37·5 mm. Hg	...	...
85	45·0 ,,	...	...
80	62·5 ,,	1·6602	0·001409
75	88·0 ,,	1·6490	
70	118 ,,	1·6382	
65	159 ,,	1·6273	
60	210 ,,	1·6167	
55	275 ,,	1·6055	
50	350 ,,	1·5945	
45	445 ,,	1·5830	
40	560 ,,	1·5720	
35	705 ,,	1·5589	
33·6	760 ,,	1·5575	
30	1·20 Atm.	1·5485	0·001793
25	1·50 ,,	1·5358	
20	1·84 ,,	1·5230	
15	2·23 ,,	1·5100	
10	2·63 ,,	1·4965	
5	3·14 ,,	1·4830	
0	3·66 ,,	1·4690	
+ 5	4·25 ,,	1·4548	0·001978
10	4·95 ,,	1·4405	
15	5·75 ,,	1·4273	0·002030
20	6·62 ,,	1·4118	
25	7·63 ,,	1·3984	0·002190
30	8·75 ,,	1·3815	
35	9·95 ,,	1·3683	0·002260
40	11·50 ,,	1·3510	
50	14·70 ,,	1·3170	0·002690
60	18·60 ,,	1·2830	
70	23·00 ,,	1·2430	0·003460
80	28·40 ,,	1·2000	
90	34·50 ,,	...	...
100	41·70 ,,	...	...
110	50·80 ,,	...	...
120	60·40 ,,	...	...
130	71·60 ,,	...	...
146	93·50 ,,	Critical point.	...

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[1] *Annalen*, 1890, **259**, 100.

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END OF PART I.

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